CHEMISTRY OF THIONITROSYL GROUP AND ITS COMPLEXES WITH RHODIUM (III)

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In Partial Fulfilment of the Requirements
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By

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INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

APRIL, 1980

TO MY
PARENTS & TEACHERS

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India under the supervision of Professor U.C.Agarwala.

In keeping with the general practice of reporting scientific observations due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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This is to certify that Mr. D. Krishna Murty Raju has satisfactorily completed all the courses required for the M.Phil. degree programme. These courses include:

Chem	501	Advanced Organic Chemistry I
Chem	521	Chemical Binding
Chem	524	Modern Physical Methods in Chemistry
Chem	541	Advanced Inorganic Chemistry I
Chem	542	Advanced Inorganic Chemistry II
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CERTIFICATE II

Certified that the work contained in this thesis, entitled "Chemistry of Thionitrosyl Group and its Complexes with Rhodium(III)" has been carried out by D.Krishna Murty Raju under my supervision and the same has not been submitted elsewhere for a degree.

U.C. Agarwala
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Thesis Supervisor

Kanpur
April, 1980

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CHAPTER I

CHEMISTRY OF THIONITROSYL GROUP

INTRODUCTION

Thionitrosyl radical with one unpaired electron unlike its homolog, viz. NO, polymerizes so readily that it is not possible to isolate it as monomer solid or liquid and even in the gaseous phase, it has only a transient existence [1]. As a result of this, the studies pertaining to the structure, bonding and the reactivity of thionitrosyl* have always been challenging and despite the large interest in the chemistry of thionitrosyl, the amount of work in this field is relatively much less and fragmentory.

Although several important reviews of the compounds containing sulfur and nitrogen [1-13], covering the chemistry of polymeric sulfur nitrides and those of sulfur-nitrogen-fluorine [14-20] have appeared in the literature, but there has been no comprehensive review exclusively on thionitrosyls. In the present review, our main aim has been to provide a comprehensive account to December 1979 of syntheses, physical properties, chemical reactions and structures of thionitrosyl, its ions and the transition metal thionitrosyl complexes.

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* In this review the term 'Thionitrosyl' is employed as a general name for the compounds of the NS group.

(a) Syntheses and General Properties

The thionitrosyl radical, like NO, H, I NO_2 and ClO_2 can also exist as NS^+ or NS^- formed respectively by loosing or gaining an electron and therefore most of its properties should be approximately similar to those of NO. The presence of NS was observed for the first time by Fôwler and Barrow in 1932 while studying the band spectrum of the emitted light after passing an electric discharge through a mixture of nitrogen and sulfur vapors. They observed a resemblance of the band spectrum with that of NO [21] and concluded the presence of NS in the mixture. A few other methods for its formation have since then been developed. These are:

(i) By passing an electric discharge through SF_6 or sulfur vapour and nitrogen [21,22,23,24]

(ii) By the interaction of sulfur vapour, H_2S or SCl_2 and active nitrogen [25,29,26,22,27]

(iii) By photolysing a mixture of COS and NF_3 28

(iv) By volatilization of $(SN)_x$ [30]

(v) By thermal pyrolysis of S_4N_4 over quartz wool and silver wool at a temperature greater than $300^\circ C$ [31]

Evidence for the formation of SN^+ and SN^- ions was provided for the first time by Dressel [32] and O'Hare [33] respectively during their spectroscopic studies. Subsequent work by other workers [34-37] led to the isolation of a

number of ionic salts containing NS^+ ion which will be discussed at a later stage in the review.

NS bond length (149.7 pm) calculated from its spectroscopic moment of inertia [38] is shorter by 24-28 pm than the sum of the single bond covalent radii of nitrogen and oxygen. It suggests the bond order of NS between two and three which is parallel to that of NO because of the similar electronic structures of NS and NO molecules (Three bonding MO fully occupied and an odd electron in the antibonding MO).

The ionization potential for the process, $NS(^2\Pi) \longrightarrow NS^+(^1\Sigma) + e^-$ at 0^oK is 9.85 e.v. [39]. This value is slightly greater or similar to that for $NO \longrightarrow NO^+ + e^-$ (9.8 e.v.) [40-41] and is lesser than that for $N_2 \longrightarrow N_2^+ + e^-$ (15.5-17.2 e.v.)* [42] or that for $O_2 \longrightarrow O_2^+ + e^-$(12.2-18.2 (12.2-18.2 e.v.)* [43]. The lower value of the ionization potential of NS than that for N_2 or O_2 and similar to that of NO reflects the loss of an odd electron from the antibonding MO of NS or NO to produce more stable ion which is isoelectronic

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* The range in the value of the ionization potentials of N_2 and O_2 is given. The exact value will depend on the electronic state of the ion (N_2^+ or O_2^+).

Table I Thermodynamic Data of NS^+, NS and NS^- [61-69]

	Total energy hartree	Ionization Potential ev	Dissociation Energy(D) ev	Dipole Moment(μ)	Quadrupole Moment $Q\times10^{-26}$ esu cm^2	ΔH_f ev
NS^+	-451.574631	24.32	5.31 $\pm$ 0.31	3.893	0.1611	12.76
NS	-451.932861	9.85	5.2 $\pm$ 0.2	1.732	-0.6734	2.91
NS^-	-451.95446	-	4.05 $\pm$ 0.2	0.09	-3.89	-

to CO or N_2. The ionic character of the NS bond (24%) calculated on the basis of Pauling's criterion [44] may be compared with that of PS bond (42%). This decrease in the ionicity of the bond parallels the difference between the electronegativities of phosphorus and nitrogen.

(b) Thermodynamic Properties

The thermodynamic properties of NS, NS^+ and NS^- have been studied both theoretically and from the spectral and thermochemical data by O'Hare [39]. The data relating to these properties are given in Table 1.

The dissociation energy of NS molecule was determined using Hildenbrand and Murad relationship [45] (4.8 e.v.) which is in excellent agreement with the one obtained by the method proposed by Gaydon [46] (4.79 e.v.). Equatioh, $D_o^o(NS^+) = D_o^o(NS) + I(S) - I(NS)$ was subsequently applied to calculate the heat of dissociation of NS^+ (5.31 e.v.).

$D_o^o/D_{LBX}^o = \frac{5.256}{r_e\ I(S)-E_a(N)} + 0.448$, where D_o^o is the true dissociation energy; D_{LBX}^o, dissociation energy determined by the Lenear Birge-Sponer extrapolation of spectroscopic data method 53 ; r_e equilibrium internuclear distance (1.4957 A for NS); I(S), ionization energy of sulfur (10.36 e.v.) and $E_a(N)$, electron affinity of nitrogen (0.04 e.v.) 54

Dissociation of NS^- ($^3\Sigma$) to give N (^4S) and S^- (^2P) involves the uncoupling of the same number of electron pairs as those in the dissociation of NO^- ($^3\Sigma$) to N (^4S) and O^- (^2P). Assuming the molecular extra correlation energy, ΔE_{cor}, to be the same for both the processes, the dissociation energy, D(NA) and the electron affinity of NA and A (where A is O, or S) were related as $D(NA^-)=D(NA) + E_a(NA)-E_a(A)$. Using the data of NO [47-52] , ΔE_{cor} was calculated for NO^- which was also assumed to be the same for NS^- (0.1333 e.v.). Combination of the Hartree-Fock energies of N (^4S), S^- (^2P) and NS^-, yielded D(NS) from which the value of $D(NS^-)$ (4.05 $\pm$ 0.2 e.v.) was calculated after the addition of ΔE_{cor}(NS) to D(NS).

Using similar relationship O'Hare has calculated the heat of formation of NS and NS^+ (Table 1). O'Hare's value of $\Delta H_f(NS^+)$ was slightly higher than that obtained by Hobrock, Shankal and Kiser [55] (10.9 e.v.). He ascribed this difference between the two value to the incorrect assumptions made by Hobrock, et.al., in their calculations.

Ab initio calculations for NS, NS^+ and NS^- based on the Hartree-Fock Roothan approach by various workers [56-60] yielded the values of the ionization potential, and the dissociation energy in excellent agreement with the ones obtained by the experimental data.

It is interesting to note the D(NS) is less than that of $D(NS^+)$. Since NS^+ has one less antibonding electron than in NS, the lower value of D(NS) is not unexpected. This type of lowering in the values of dissociation energies of the singly + vely charged species was also observed in other diatomic molecules which are isoelectronic with NS e.g. SiF, PO, CCl etc. The same trend is also observed in the values of this ionization potentials of NS and NS^+.

The Electronic Structure of NS and Related Compounds

It is interesting that in contrast to its homolog, NO, having the same number of valence electrons, thionitrosyl molecule has only a transient existence in the gaseous phase. In solid or liquid phase it polymerizes too readily into S_2N_2, S_4N_4 and $(SN)_x$ and is therefore not possible to isolate it. Further, S_2N_2, unlike N_2O_2, a colourless crystalline solid, is highly explosive if not pure and undergoes polymerization into $(NS)_x$ via S_4N_4. The geometries of these molecules are summerized in Table II. Several attempts [24-26,64,70-72] have been made to understand the electronic factors which lead to such a behaviour of NS.

Monomer NS is a paramagnetic molecule having a doublet $^2\Pi_{1/2}$ ground state with the lowest excited state, $^2\Pi_{3/2}$ lying 223 cm^{-1} above the ground level. A calculated electronic configuration of the ground state of NS is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$ where the valence electrons of only nitrogen and sulfur are considered. In the molecular orbital description of NO $3\sigma^2$ and $1\pi^4$ levels are reversed, although the energy distance between them ($3\sigma^2$ and $1\pi^4$) is small in both the molecules [73]. The calculations indicate that the sulfur d-orbital participation in the bond formation of NS is small ($<10\%$). With the result its effect on orbital energies is less than 0.3 e.v. (Fig. 1). However, for S_2N_2 the extent of d orbital participation is relatively larger though still of minor importance. A charge distribution analysis in each of the MO as well as the total charges on sulfur and nitrogen in SN shows that the charges in the sulfur and nitrogen spheres are within a few percent of each other for all the molecular orbitals. Consequently, since the number of valence electrons on atomic sulfur is one more than that on atomic nitrogen, a net charge transfer (equivalent to approximately 0.5 electron) takes place from sulfur to nitrogen, which is in comformity with the electronegativity values of sulfur (2.5) and nitrogen (3.0). It will, thus, lead to a high value of the dipole moment of SN ($\overset{\delta+}{S} - \overset{\delta-}{N}$) (Experimental value of dipolemoment of SN is 1.86 D [68] . The situation in NO is just opposite

to that of NS. The charge distribution in nitrogen and oxygen spheres in NO is less even and the calculated value of charge transfer is approximately equivalent to 0.32 electrons. This will result in a lower value of dipole moment of $\overset{\delta-}{N} - \overset{\delta+}{O}$ [the observed value of dipolement of NO is 0.16D]. The direction of dipole moment of NO is opposite to what one would expect on the basis of the electronegativity values of nitrogen (3.0) and oxygen (3.5). Hartree and Fock calculations [74,75] predicted that the dipole moment of NO will be small and of opposite sign to that predicted by methods which include correlation effects. Thus, the dipole moment of NO depends on the detailed behaviour of electrons rather than on the net electronic charge in a some what arbitrary volume around each nucleus.

The structure of S_2N_2 (a planer square with alternating sulfur and nitrogen atoms and a bond distance of 1.65 A) could be due to aligning of two $\overset{\delta+}{S} - \overset{\delta-}{N}$ molecules in such a way that the two dipoles interact in an electrostatically favourable manner. This type of alignment will not be stable in case of N_2O_2 which is actually a loosely bond trapezoidal arrangement of N and O with the shortest distance (2.18 A) between two nitrogen atoms [76,84] . Despite the chemical binding in S_2N_2 is more complex than the simple dipolar interaction, it seems that one of the main factors controlling

the relative geometry of S_2N_2 and N_2O_2 is electrostatic in nature. A charge distribution study in S_2N_2 shows a net charge transfer of 0.48 electron per atom from S to N. A CNDO/2 localized MO study of S_2N_2 leads to the conclusion that the molecule is formed from σ electrons in three center bonds and four unshared pairs of electrons superimposed on a square planer (D_{2h} symmetry) bond structure [82-84]. The physical and chemical properties of disulfur dinitride have been subject of several studies [85-110].

A considerable amount of work (both theorectical and experimental) has been done on the structure of S_4N_4 [111-131]. It is now generally agreed that S_4N_4 has a structure with four coplanar nitrogen atoms and four sulfur atoms alternatively above and below the plane. However, the question of the electronic structure and the nature of bonding are still open. Various workers [118-121] have found a different net charge transfer from sulfur to nitrogen (0.328-0.56 electron) All the methods indicate substantial S-S orbital overlap and little or practically no N-N bonding interaction. All the studies of the sulfur nitrides relating to their structure lead to polar bonds in them. It, further, appears that in the polymerization process of SN to $(SN)_x$ bond dipolar forces determine the geometry of the dimer, S_2N_2 which is then

thermally excited to a low lying high spin state and the chain propagation takes place as a result of interaction of these excited species followed by their rearrangements to yield $(SN)_x$ structure.

(d) Spectroscopic Properties of NS

A large number of papers related to the microwave spectra of NS have appeared in the literature [132-165] In 1932 Fowler and Bakker [21] have discovered the A_x and C_x systems of NS radical in the light emmitted by an electric discharge through a mixture of nitrogen and sulfur vapour. Subsequently there have been a number of other investigations in the course of which the excited valence states $B^2\Pi$, $A^2\Delta$, $G^2\Sigma^-$, $H^2\Pi$ and $I^2\Sigma^+$ have been identified besides the ground $X^2\Pi$. Rosen has compiled

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* The dipolemoments of NS^- and NS^+ are 0.09D [33] and 3.893 D respectively. The change of dipole moments of NS from 1.84D (theoritical 1.73D [68] to 0.09D for NS^- is consistent with the addition of one electron primarily at the sulfur end of the molecule .

all the spectroscopic data of NS molecule upto 1969 in the book "Spectroscopic Data relative to diatomic molecules." Furthermore a low lying $2\Sigma^{+}$ has also being reported which has been named as β state. The observed states, X, B, A, G, H and I are associated respectively with the theoretical states $2\Pi(1)$, $2\Pi(2)$, $2\Delta(1)$, $2\Sigma^{-}(1)$, $2\Pi(3)$ and $2\Sigma^{+}(2)$.

The electronic emission spectrum of NS has been discussed by Joshi, et.al. [22] . The electronic states of NO and NS are shown in Fig. II.

The i.r. spectra of NS radical showed a very weak band at 1225 cm^{-1} [30] (the vibration frequency of the gaseous NS molecule [70,166,167] is given as 1204.1 cm^{-1}).

Very little information is available in the literature concerning the ionic state of NS, the only ionic state to be even partially characterized is the ground state, Σ^{+}. The band associated with the first ionization potential of the NS molecule corresponding to the ionization $NS^{+}(X^{1}\Sigma^{+})$ —— $NS(X^{2}\Pi)$ has been observed by photoelectron spectroscopy using HeI and NeI photon sources [160]. The vertical ionization of this band has been measured as 8.87 ± 0.01 e.v. and the position of three vibration components associated with this band leads to $W_e = (1415 \pm 20)\ cm^{-1}$ and $W_eX_e = (15 \pm 10)\ cm^{-1}$ for the NS^{+} ($X^{1}\Sigma^{+}$ state). The

increased value of We compared with the neutral molecule value of 1219 cm^{-1} [72] is, as expected, consistent with removal of an electron from an antibonding orbital and is directly analogous to the corresponding increase in vibrational frequency on going from $NO(X^2\Pi)$ to $NO^+(X^1\Sigma^+)$

The potential energy diagram (Fig.III) has been constructed by using all the NS^+ $(^1\Sigma^+)$ parameters . An average of the parameters of the $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ states has been taken [72] in drawing this diagram. Also values of the dissociation energy and first ionization potential of $S(^3P)$ have been taken as (4.87 ± 0.25) ev [38,64] and 10.357 eV [63] respectively.

(e) Electron Paramagnetic Resonance

Carrington,et.al., first observed the electron paramagnetic resonance spectrum of NS obtained by the action of nitrogen atoms with hydrogen sulphide in a spectrophotometer cavity, [169-171] and by reacting N-atoms with S_2Cl_2 [66]. Uehare and Merino [172] have detected an intense electron paramagnetic resonance spectrum of NS in the gas phase by passing a mixture of N_2 and SCl_2 through a microwave discharge cavity and then through a spectrometer cavity. The electron paramagnetic resonance spectrum of NS

consists of three triplets and the position of the centre of the spectrum indicates a g factor close to 0.8 (the value expected for a molecule in a $^2\Pi_{3/2}$ state in the lowest rotational level with J=3/2). The analyses of ultraviolet spectrum of NS shows that the ground state is actually $^2\Pi_{1/2}$ state. The electron spin g factor g_e of NS lies probably between the free spin g factor and the electron spin g factors for O_2 [173] or for SO[174]. (Fig.IV) NS radical would be expected to have an electronic structure similar to that of NO and molecular parameters for the two species are compared in Table III.

Table II. Geometries of SN, S_2N_2 and S_4N_4

		r_{SN}	SNS	NSN
SN	$C_{\infty v}$	1.495	-	-
S_2N_2	D_{2h}	1.620	95	85
S_4N_4	D_{2d}	1.616	113	105

Table III. Molecular Parameters for NS and NO

	NS	NO
Rotational constant B_o	0.7724 cm^{-1}	1.6957 cm^{-1}
Fine structure constant A	223.0(3) cm^{-1}	123.160$\pm$0.02 cm^{-1}
Hyperfine constant h	56.8$\pm$0.5 MHz	75.81 $\pm$0.24 MHz
Quadrupole coupling constant Q	3.1$\pm$0.5 MHz	1.8 $\pm$0.3 MHz
Dipolemoment u	1.732 D	0.158$\pm$0.005 D

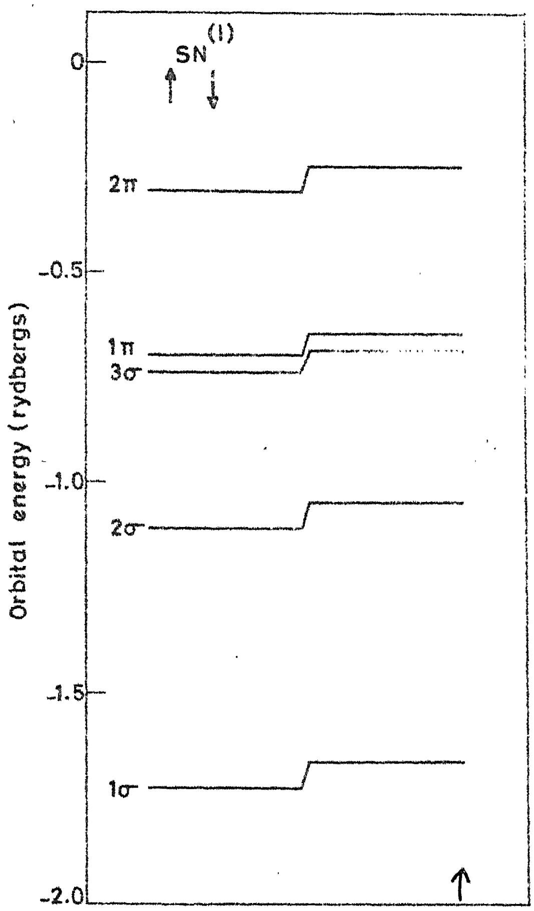


Fig. I Orbital energies for the molecular orbitals of NS.

↑ → d- orbital contribution

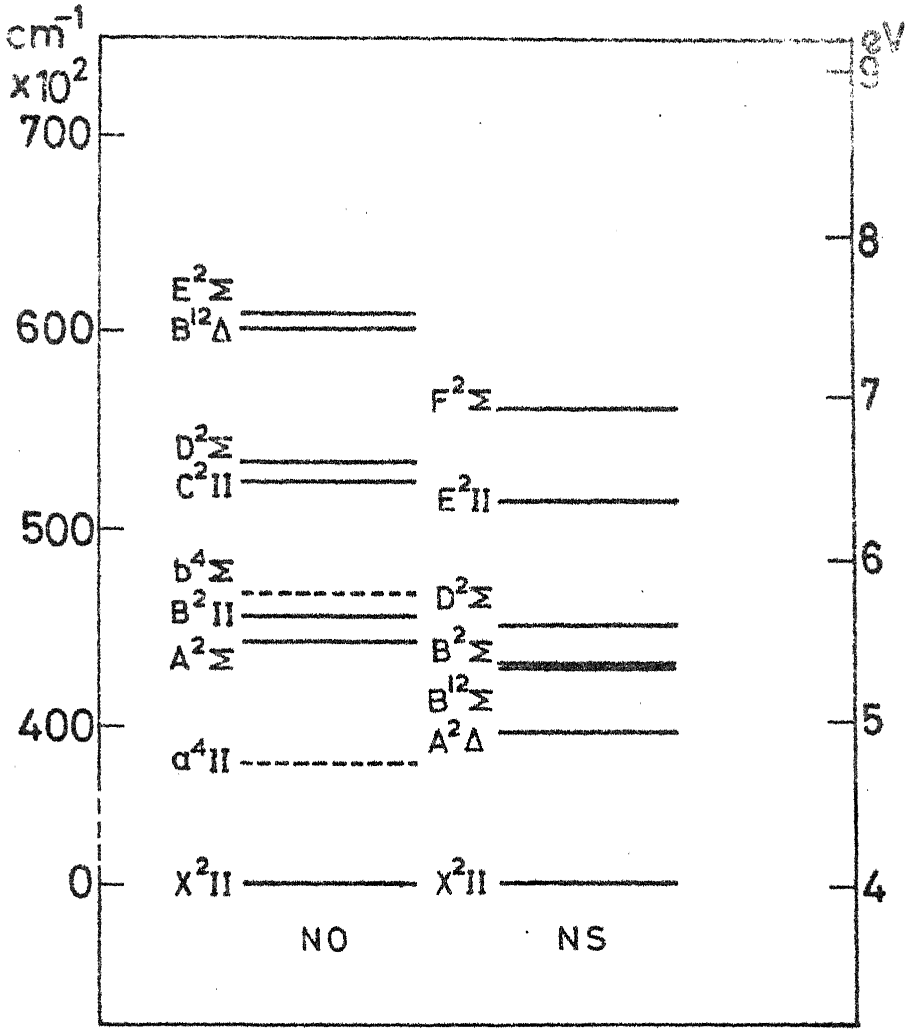


Fig. II Electronic states for NO and NS molecules.

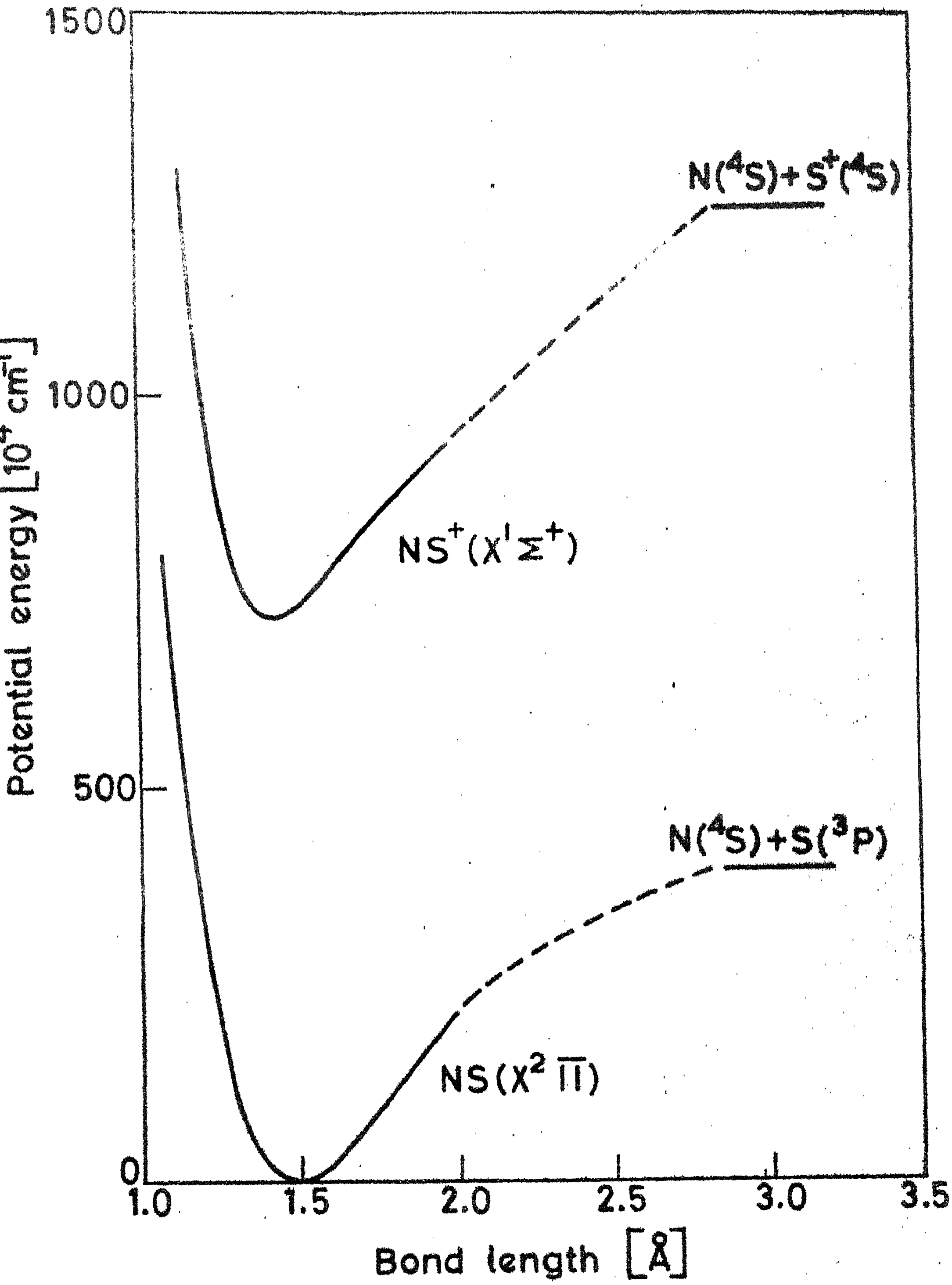


Fig. III Potential energy diagram

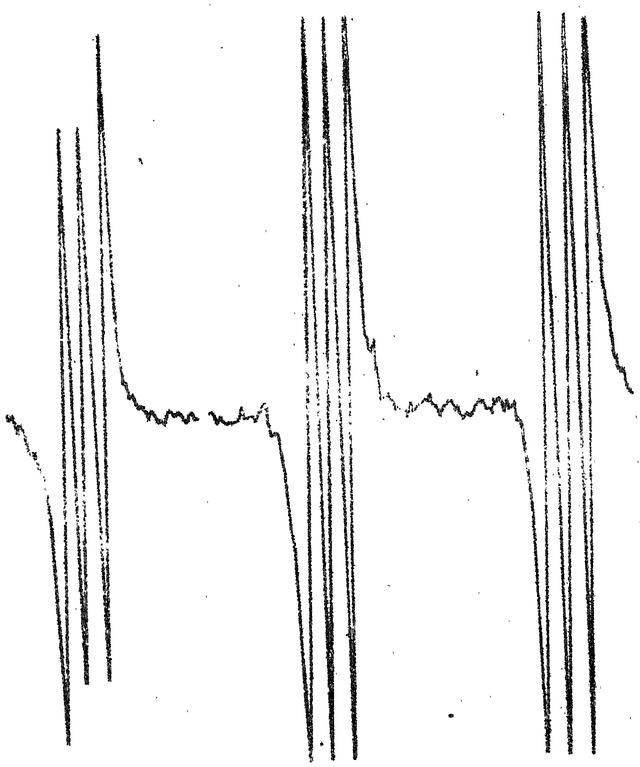


Fig. IV EPR spectrum of NS.

Ionic Compounds

In 1971 Glemser and Koch [34,35] for the first time obtained the ionic compound of NS^+ by the reaction of NSF with AsF_5. A number of other methods for the syntheses of such salt like compounds have since then been developed. The best results were achieved by reacting NSF with the Lewis acids MF_5 [M=As or Sb] or BF_3 in the gaseous phase at reduced pressure [36,37,175]. For preparative purposes these salts could best be synthesized by the reaction of NSF with MF_5 in liquid SO_2. A yield upto 90-100% can be attained by this method.

The thionitrosyl compounds, $[NS]^+ [AsF_6]^-$, $[NS]^+[SbF_6]^-$ or $NS^+BF_4^-$, were also obtained by the action of tri or tetramer of NSF with an excess of AsF_5, SbF_5 or BF_3 respectively [176].

$$N_3S_3F_3 + MF_5 \longrightarrow N_3S_3F_2^+ MF_6^- \text{ (M=As or Sb)} \tag{1}$$

$$N_3S_3F_2^+ MF_6^- \xrightarrow[180^\circ C]{} NS^+MF_6^- \tag{2}$$

or $$N_3S_3F_3 + BF_3 \longrightarrow N_3S_3F_2^+BF_4^- \tag{3}$$

$$N_3S_3F_2^+BF_4^- \longrightarrow NS^+ BF_4^- \tag{4}$$

and $$N_4S_4F_4 + MF_5(\text{or } BF_3) \longrightarrow N_4S_4F_3^+ MF_6^- \text{ or } BF_4^- \tag{5}$$

$$N_4S_4F_3^+ MF_6^-(\text{or } BF_4^-) \longrightarrow NS^+MF_6^- (\text{or } BF_4^-) \tag{6}$$

Purification of $NS^+AsF_6^-$ can be affected by subliming the crude product at 40°C under reduced presure whereby a stable colourless waxy solid which can be kept without decomposition for years in dry glass vessel, was obtained. The purification of $NS^+SbF_6^-$ was accomplished by heating it at 100°C and the residue, thus left, is crystallized either from liquid SO_2 or from SO_2ClF. Tetrafluoro derivative is not stable even at low temperatures and it could, therefore, not be purified by recrystallization.

The ionic nature of these compounds was confirmed by the following experimental techniques.

(a) <u>Raman spectra</u> : The Raman spectra of all these salts showed one band in the region 1435 cm^{-1} which was assigned to $\gamma_{(NS)}$. This band appeared in the spectrum of NSF at a lower frequency (1372 cm^{-1}). From these band positions the valence field force constants** of the NS and its bond order were calculated. The results indicate a considerable strengthening of NS bond in NS^+ salt like compounds, which further confirms the ionic nature of the salts. The frequencies of some of the compounds are shown in Table IV.

** $f(NS^+)$ in NS^+AsF_6=11.85 Dynes/A° f(NS) in NSF=10.71 Dynes/A°
Bond order, $n(NS^+)$=2.6 Bond order of NS; nNS=2.4

(b) NMR Spectra: There appeared no signal of F^{19} between +350 to -440 ppm, characterstic to SF. It has therefore been assumed that there is no bond between sulfur and fluorine.

(c) Exchange Reactions: The lack of exchange of F^{19} between the anions of these compounds and (AsF_6^-) further confirm the ionic nature of the compounds.

Since attempts to obtain a single crystal of these compounds failed, no single crystal x-ray structural studies was thus far reported in the literature.

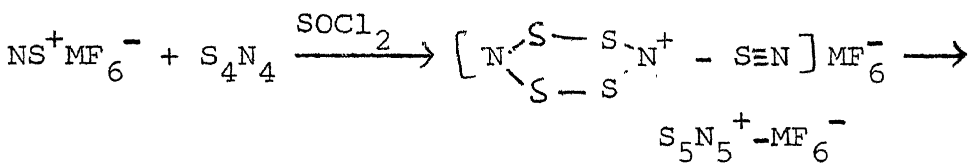
Thionitrosyl salts have been used to introduce thionitrosyl group into other molecules. Synthetic possibilities by these ionic compounds include reactions with anions, nucleophiles and with compounds having polar bonds. Thus,

(i) Reaction of thionitrosyl cation with anions

The reaction of $NS^+AsF_6^-$ with $NO^+(CF_3SO_3)^-$ in liquid sulfurdioxide yielded a colourless product, $NS^+[CF_3SO_3]^-$ (m.p. 120°) which was purified by sublimation (30°C/0.01 torr). It was extremely hygroscopic and sensitive to hydrolysis. The ease of sublimation was taken as an indication for its being monomer at least in the gaseous phase. The presence of a band in its Raman spectrum due to ν_{NS^+} at 1443 cm^{-1} is in support of its being an ionic compound.

(ii) Reaction of thionitrosyl cation with nucleophiles

Insertion of NS unit into S_4N_4 gives yellow pentathiazyl salts in the yields of about 80%. Thus,



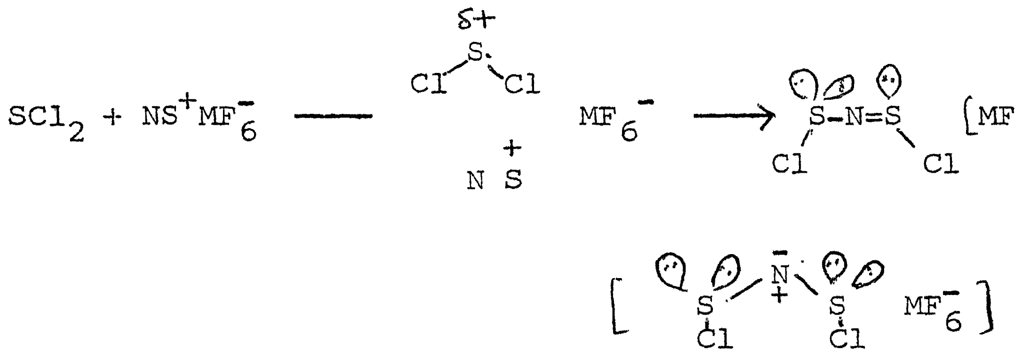
(7)

M=As(yellow solid m.p. 267°C) or Sb (yellow solid,m.p.175°C)

The formulation of the intermediate product in these reactions is quite arbitary because both are simply addition of the nucleophile, S_4N_4, to sulfur of $\overset{+}{NS}$: to form either linear cationic thiazenes or a cyclo addition product of $\overset{+}{NS}$: to S_4N_4. When the same reaction was carried out in liquid SO_2, the reaction product was a black solid, $(S_5N_5)^+AsF_6^-$ (dec 110°C) together with other unidentified substances. The i.r. spectrum of $S_5N_5^+AsF_6^-$ showed a strong band at 700 cm^{-1} characterstic of AsF_6^- group and a broad band at 850 cm^{-1} indicating its polymeric nature. The ratio of NS:AsF_6 in the black compound can be varied by changing the stoichiometry of the reacting species. A drop in this ratio (increase in charges of the polymer) was associated with a shift of position of ν_{NS} band towards higher wave numbers.

(iii) <u>Reaction of the thionitrosyl cation with polar bonds</u>

The reaction of S_2Cl_2 with $NS^+MF_6^-$ gave $N(SCl_2)^+MF_6^-$ (M=As or Sb) according to the following reaction :



(8)

The synthesis of the cation, $[N(\underline{S}Cl_2)]^+$ [177] was first accomplished as tetrachloroborate from the reaction of NSF_3 and BCl_3. It can also be obtained from SCl_2, $(NSCl)_3$ and MCl_3 [178,179] . Thus ,

$$S_3N_3Cl_3 + 3SCl_2 + 3MCl_3 \longrightarrow 3[N(SCl)_2]^+[MCl_4^-] \qquad (9)$$

M = Al, Sb, As

The compound $[N(SCl)_2]^+[MF_6]^-$ which can be regarded as derivative of : ClSN = SCl_2 or ClSN = SClF , decomposes on reacting with NOCl.

The reaction of $NS^+ MF_6^-$ with SCl_2 can be generalized for sulfenyl chloride. Thus, the salts $[CF_3SNSCl]^+[MF_6^-]$ and $[(CF_3)_2 C{=}N{-}SNSCl]^+ MF_6^-$ were prepared by reacting $NS^+ MF_6^-$ with CF_3SCl and $(CF_3)_2 C{=}N{-}SCl$ respectively [180] .

Table IV. Thionitrosyl Cations

	m.p. ^{o}C	Colour	Raman frequency ν_{NS} cm^{-1}	Reference
$NS^{+}AsF_6^{-}$	-	Colourless	1437	34,35
$NS^{+}SbF_6^{-}$	-	Colourless	1448	175
$NS^{+}BF_4^{-}$	-	Colourless	-	36,37
$NS^{+}CF_3SO_3^{-}$	$120^{o}C$	Colourless	1443	175
$NS^{+}AlCl_4^{-}$	-	-	-	181
$NS^{+}FeCl_4^{-}$	-	-	-	181
$NS^{+}GaCl_4$	-	-	-	181

Covalent Compounds

The chemistry of the compounds containing nitrogen sulfur and halide (halide = Cl or F)is mainly concerned with the covalent compounds of thionitrosyl. There are three principal covalent compounds of NS viz. NSF, NSF_3 and NSCl which we shall discuss here.

Thionitrosyl Fluoride NSF

The literature methods of synthesizing this compound are

(a) Fluorination of compounds containing NS bonds

AgF_2 [36,182], COF_3 [36] and HgF_2 [183] can fluorinate S_4N_4 producing NSF.

$$S_4N_4 + 4HgF_2 \xrightarrow[\text{Reflux}]{CCl_4} 4NSF + 2Hg_2F_2 \qquad (10)$$

Other compounds used as fluorinating agents are SeF_4, F_2 184, SF_4 (184,185), IF_5 and SbF_5. The latter two agents give first adducts, viz $(NSF)_4S_4N_4$ or $S_4N_4(SbF_5)_4$ which gave NSF when they are thermally decomposed [186].

(b) By reacting SF_4 with NH_3

$$SF_4 + 4NH_3 \xrightarrow[\text{streaming}]{20^{\circ}} NSF + 3NH_4F \qquad (11)$$

$$S + 4AgF_2 + 4NH_3 \xrightarrow[CCl_4]{} NSF + 3NH_4F + 4AgF \qquad (12)$$

(c) By reacting NF_3 with sulfur or metal sulfide [188-190]

$$NF_3 + 3S \xrightarrow{350-400} NSF + 2SF_2 \qquad (13)$$

$$MOS_2 + NF_3 \xrightarrow{280} NSF + MOF_3 \qquad (14)$$

$$NF_3 + COS\ (\text{or } CS_2) \xrightarrow[\text{photolysis}]{\text{flash}} NSF \qquad (15)$$

In the course of these reactions other side products difficult to seperate were also obtained. Maximum yield was found to be 20-30%.

(d) By decomposition of compounds containing NSF group [36,191-192]

$$S_4N_4F_4 \xrightarrow[\text{Reflux}]{CCl_4} 4NSF \qquad (16)$$

$$COF\ NSF_2 \xrightarrow[C_5F]{20^oC} COF_2 + NSF_2 \qquad (17)$$

$$Hg(NSF_2)_2 \xrightarrow[\text{High vacuum}]{110^o} 2NSF + HgF_2 \qquad (18)$$

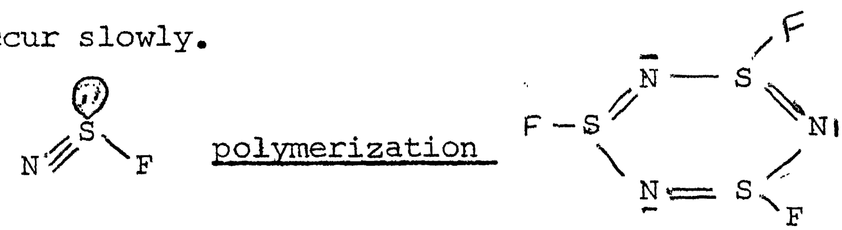
The last reaction is suitable for the preparation of NSF in the large quantities.

Thionitrosyl fluoride (m.p. -89°C, b.p. 0.4°C) is a pungent smelling and pale yellow liquid. It is hydrolysed with water to give NH_3, sulfite and fluoride ion probably via unstable intermediate, thionylimide [194] .

$$NSF + OH^- \longrightarrow NSOH + F^- \longrightarrow HNSO + F^- \qquad (19)$$

$$NSOH + 2H_2O \longrightarrow NH_4^+ + SO_3^{--} \qquad (20)$$

The hydrolysis of NSF with dilute NaOH yielded first a yellow precipitate which was dissolved rapidly. It can not be stored at room temperature in glass vessels owing to its decomposition into N_2, SOF_2, SiF_4 and $(NSF)_3$. In teflon or copper containers it is relatively stable in liquid state but their trimerization also occur slowly.



(21)

In gaseous state at reduced pressure S_4N_4 or $S_3N_2F_2$ are the products of decomposition [195,196] .

Other reactions of NSF are given below :

(i) $NSF + AgF_2 \xrightarrow{20-100^{o}} NSF_3$ [36,197] (22)

(The reaction can be used to prepare NSF_3)

(ii) $NSF + CsF \xrightarrow{Cl_2(gas)} ClNSF_2$ [192] (23)

(iii) $NSF + CsF \xrightarrow{CH_3CN} Cs^+ (NSF_2)^-$ [198] (24)

Reactions (ii) and (iii) illustrates the transformation of NSF into NSF_2.

(iv) $NSF_2 + Cl_2 \longrightarrow NSCl \longrightarrow 1/3\ N_3S_3Cl_3$ (25)

(v) $NSF + SbF_5/AsF_5 \longrightarrow NSF.SbF_5$ or $NSF.AsF_5$ (26)

(vi) $NSF + BF_3 \longrightarrow NSF\,BF_3$ 36,37 (27)

Reactions (v) and vi) are used in the preparation of ionic compounds of NS^+ (see section on Ionic compounds)

(vii) The thionitrosylfluoride (NSF) is decomposed by HF [199]

$$NSF \xrightarrow{HF} H\text{-}N{=}SF_2 \xrightarrow{HF} H_2N\text{-}SF_3 \xrightarrow{HF} NH_4F + SF_4 \quad (28)$$

(viii) The thionitrosylfluoride lose F^- and goes over to thiazyl cation

$$NSF \xrightarrow{-F^-} NS^+ \quad [19] \quad (29)$$

(ix) γ-irradiation of NSF in SF_6 give probably NSF_2 and FNSF radicals [200] .

Kirchhoff and Wilson [201] determined the molecular parameters from IR, NMR, microwave studies and proposed structure I . It was further confirmed by LCAO MO ab initio studies [202] and CNDO/2 calculations [203] . These results do not agree with the structure II and III proposed by Glemser, et.al. [204] from their studies and supported by Rogowski [205] on the basis of electron diffraction studies. Duke [202] recently observed that NSF is more stable than SNF. The observed S-F distance is 1.585A in $SOCl_2$, 1.53A in sulfunyl fluoride [206] , 1.58A in SF_6, 1.50A in S_2F_{10} and N S distance 1.416A in NSF_3. It is evident from these

results that S-F and N S distances in thionitrosylfluoride are significantly larger than the ordinary single and triple bonds.

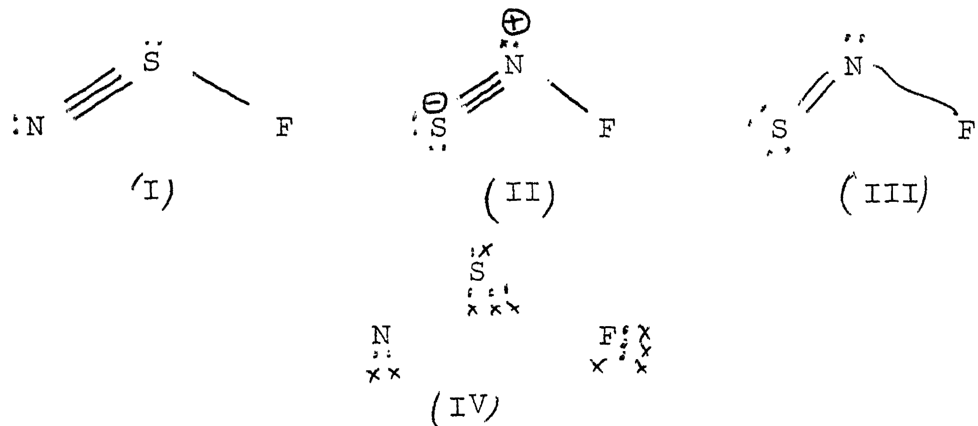


Fig. V

The NS force constant f(NS) calculated from microwave and IR data has a value 10.7 mdyne/A$^{\circ}$ [207-209] from which a bond order of 2.4 was calculated [210]. For NSCl having similer structure, f(NS) is found to be 10.0 mdyne/A$^{\circ}$ and bond order, 2.2 [211] . Thus, NS bond order depends upon the electronegativity of the element attached to sulfur which therefore suggests d - p bonding between N and S. Since then structure IV was proposed based on the hypothesis of Linnett [212] . This structure is thought to be the most stable configuration of NSF in the ground state as the doublet quartet of electrons [213] . The 'dots' represent the electrons with spin quantum number of +1/2 and the 'crosses', the electrons with spin quantum number of -1/2

or vice versa. Both spin sets of nine electrons favour a bent configuration. The two sets of four electrons around each nucleus can be treated as being uncorrelated and spatially related to one another. The electrostatic repulsion and the Pauli-principal effect cancel one another as far as the spatial correlation of the two sets is concerned. The electrons are widely separated in structure IV than they are in other structures.

The enthalpy of formation ΔH_f(NSF) gas, 298-15K) 41 ± 2 kcal mole^{-1} [213] is derived from $\Delta H_f(NSF_3$, gas, 298.15°K) and the mass spectrometric appearance potentials [214]. The dissociation energy D_{NS}(NSF) = 71 ± 5kcal mole^{-1} [213]; dipole moment 1.902D [207]. NMR and electronic spectral studies of NSF [215] have also been carried out.

Thionitrosyl Trifluoride NSF_3

NSF_3 is the first compound with N-S triple bond and in which nitrogen and fluorine, together share six covalent bonds with sulfur.

NSF_3 can be synthesized (a) by fluorination of N-S compounds containing sulfur in +4 or lower oxidation state and (b) by the reaction of S^{+6}-F compounds with excess of ammonia. It can thus be obtained,

(a_1) by refluxing tetrasulfurtetranitride with silver difluoride in carbon tetrachloride [36,183,197]

$$S_4N_4 + 12AgF_2 \xrightarrow[\text{reflux}]{CCl_4} 4NSF_3 + 12AgF \qquad (30)$$

(a_2) by fluorination of thionitrosyl fluoride with the silver difluoride [36,183,197,216]

$$NSF + 2AgF_2 \longrightarrow NSF_3 + 2AgF \qquad (31)$$

(a_3) by the reaction of $COFNSF_2$ with AgF_2 [198] (32)

$$OCFNSF_2 + AgF_2 \xrightarrow{20^\circ} NSF_3 + COF_2 + 2AgF \qquad (33)$$

(b_1) by passing ammonia into a suspension of sulfur and AgF_2 in CCl_4

$$NH_3 + S + 6AgF_2 \xrightarrow{CCl_4} NSF_3 + 3HF + 6AgF \qquad (34)$$

and (b_2) by reducing S_2F_{10} with excess of ammonia [216,218]

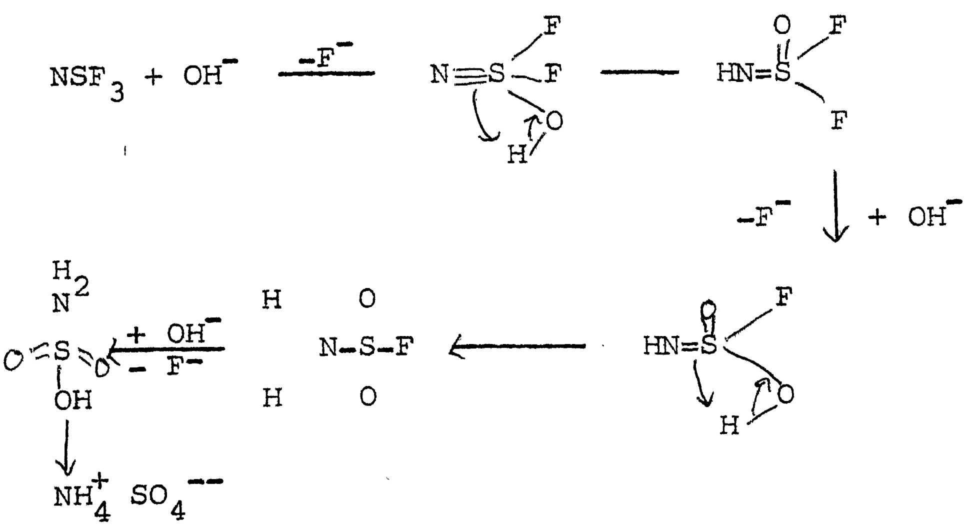
$$S_2F_{10} + NH_3 \xrightarrow{150^\circ} NSF_3 + SF_4 + 3HF \qquad (35)$$

The last method of synthesizing NSF_3 is in particular not very much employed because of high toxicity of S_2F_{10} and of the low yield.

Thionitrosyltrifluoride is a colourless, pungent smelling gas (m.p. -72.6° ± 0.5, b.p. -27.1° ± 0.1°). Its enthalpy of formation and dissociation energy D(N≡S) are 85 kcal mole^{-1} and 93 ± 2 kcal mole^{-1} respectively [224]. It is thermally and chemically very stable because of which its use as dielectric has been suggested [219]. It decomposes only above 500°C in glass vessels to give sulfur, SO_2, nitrogen, SiF_4 and metallic fluorides as decomposition products [36]. It is unaffected by metallic sodium upto 300°C and unlike NSF it is not hydrolysed by dilute mineral acids.

The important reactions of NSF_3 are as follows:

(a) It is hydrolysed by water or by a strong alkali. In this reaction proton migration is suggested if a sulfur oxygen double bond can form at the expense of a sulfur-nitrogen multiple bond [220].



(36)

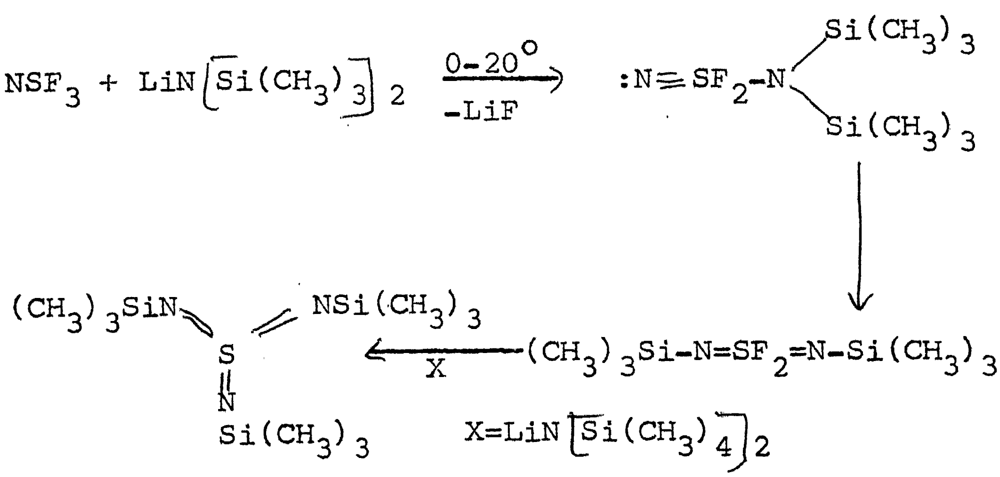
(b) It forms adducts with Lewis acids, like BF_3, MF_5(M=As,Sb) [35,37,221]

$$NSF_3 + BF_3 \longrightarrow F_3B - NSF_3 \qquad (37)$$

$$NSF_3 + MF_5 \longrightarrow F_5M - NSF_3 \qquad (38)$$

In gaseous phase these adducts dissociate into their components. Their i.r. spectra show a shift in the position of $\nu_{(NS)}$ towards higher wave numbers by about 200 cm^{-1} which is due to the increase in the N—S bond order from 2.7 to 2.9.

(c) It reacts with $LiN[Si(CH_3)_3]_2$ to yield $(CH_3)_3Si{-}N{=}SF_2{=}N{-}Si(CH_3)_3$ [222] which further reacts with one more molecule of $LiN[Si(CH_3)_3]_2$ resulting in the splitting of two fluorine atoms attached to sulfur and the formation of the aza analogue of SO_3 [222].



(39)

(d) The fluorine atom of NSF_3 can be exchanged with $-NR_2$ or $-OR$ group while retaining its N–S bond [223].

$$NSF_3 + 2R_2NH \xrightarrow[\text{ether}]{20^\circ} NSF_2\text{-}NR_2 + R_2NH.HF \qquad (40)$$

$R = C_2H_5$ [224], piperidine [223]

$$NSF_3 + ROH + (CH_3)_3N \xrightarrow{0-20} NSF_2\text{-}OR + (CH_3)_3N.HF \qquad (41)$$

$R = C_6H_5$ [223]

(e) Boron trichloride reacts with NSF_3 with the formation of an ionic compound, $[N(SCl)_2]^+[BCl_4]^-$

$$2N\equiv SF_3 + 3BCl_3 \xrightarrow{20^\circ} [N(SCl)_2]^+[BCl_4]^- + \tfrac{1}{2}N_2 + \tfrac{3}{2}Cl_2 + 2BF_3 \qquad (42)$$

Although this reaction is not well understood mechanistically, but possibly it proceeds via an adduct formation followed by F-Cl exchange on sulfur and reduction of NSF_3 to NSCl. The following syntheses of this compound support the reaction path

$$\left.\begin{array}{l} S_3N_3Cl + 3BCl_3 + 3SCl_2 \\ S_3N_2Cl_2 + Cl_2 + BCl_3 \end{array}\right\} \longrightarrow [N(SCl)_2]^+[BCl_4]^- \qquad (43)$$

(f) Coordinatively unsaturated transition metal complexes react as Lewis acids and add electrophillically [224,225]

$$M(CO)_5Br + Ag^+AsF_6 \xrightarrow[-AgBr]{NSF_3} M(CO)_5^+AsF_6^- \qquad (44)$$

$$M(CO)_5^+AsF_6^- \xrightarrow{NSF_3} [M(CO)_5NSF_3]^+[AsF_6]^-$$

(M = Mn, Re)

These reactions are better carried out in liquid SO_2, and in presence of only a small excess of NSF_3 e.g [225]

$$C_5H_5Fe(CO)_2I + AgAsF_6 \xrightarrow[-AgI]{SO_2} [C_5H_5Fe(CO)_2SO_2]^+[AsF_6]^- \qquad (45)$$

$$[C_5H_5Fe(CO)_2SO_2]^+[AsF_6]^- \xrightarrow[-SO_2]{NSF_3} [C_5H_5Fe(CO)_2NSF_3]^+[AsF_6]^-$$

The thionitrosyltrifluoride complex $[M(CO)_5NSF_3]^+[AsF_6]^-$ (M = Re) is a colourless crystalline solid. The IR data of thionitrosyltrifluoride and a few of its coordination compounds are given in Table V.

Table V

	NSF_3	F_5AsNSF_3	F_5SbNSF_3	$[Re(CO)_5NSF_3]^+[AsF_6]^-$	$[Mn(CO)_5NSF_3]^+[AsF_6]^-$	$[C_5H_5Fe(CO)_2NSF_3]^+[AsF_6]^-$
ν_{NS} (cm^{-1})	1515m	1650	1650	1636	1637	1632
ν_{SF} (cm^{-1})	811	950	955	900	882	888
	775	889	900	889	838	876
				846		830

(g) Polar molecules like HF, ClF, etc can be added to N$-$S bond in NSF_3 :

$$NSF_3 + 2HF \longrightarrow SF_5NH_2 \quad 226 \tag{46}$$

$$NSF_3 + ClF \longrightarrow SF_5NCl_2 \quad 227 \tag{47}$$

Because of the high polarity of these molecules ($\overset{\delta+}{H^+}-\overset{\delta-}{F^-}$, $\overset{\delta+}{Cl^+}-\overset{\delta-}{F^-}$) the first step in these reactions possibly include the addition of the cation to nitrogen followed by neutralization of this cation by F^- to form mono addition product,

$$NSF_3 + \overset{\delta+}{X^+}-\overset{\delta-}{F^-} \longrightarrow XN{=}SF_3\ F^- \longrightarrow X{-}N{=}SF_4 \tag{48}$$

These monoaddition products were, however, not isolated. It appears that the tetrafluorideimide adds a further X-F molecule with the formation of a hexacoordinated anion

$$X{-}N{=}SF_4 + \overset{\delta+}{X^+}-\overset{\delta-}{F^-} \longrightarrow X\ddot{N} \longrightarrow SF_5^- \quad X^+ \longrightarrow \begin{matrix} X \\ X \end{matrix}\!\!>\bar{N}-SF_5 \tag{49}$$

The compound SF_5NSF_2 was also isolated as a result of the reaction of NSF_3 with SF_4 in the presence of BF_3 [216] . In this reaction the addition of the SF_3^+ cation to nitrogen has been proposed as the primary step in the reaction mechanism.

$$SF_4 + BF_3 \longrightarrow :SF_3^+BF_4^- + NSF_3 \longrightarrow F_3S\text{-}N{=}SF_3^+BF_4^-$$

$$F_3S\text{-}N{=}SF_3^+BF_4^- \longrightarrow BF_3 + F_3S\text{-}N{=}SF_4 \quad (50)$$

$$BF_3 + F_3S\text{-}N{=}SF_4 \xrightarrow{\sim} F_2S{=}N\text{-}SF_5$$

The primary cation, thus, formed should be unstable under the reaction conditions and it therefore takes F^- ion from the anion to form neutral $F_3S\text{-}N{=}SF_4$. Disproportionation then leads to $SF_5\text{-}N{=}SF_2$.

(h) The nitrogen of the thionitrosyltrifluoride is protonated by HCl in the presence of $AgAsF_6$ [228]

$$NSF_3 + HCl + AgAsF_6 \xrightarrow[-AgCl]{SO_2} [HN{=}SF_3]^+[AsF_6]^- \quad (51)$$

(i) $LiN(SiMe_3)(CMe_3)$ reacts with NSF_3 to give $S(NSiMe_3)(:NCMe_3)_2$ and $S(:NCMe_3)_3$ [229].

Structure

The structure of NSF_3 (Fig.VI) has been determined from the IR [209, 230], Raman [231], NMR [209] and microwave spectra [232].

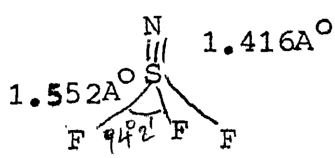


Fig VI

The NMR absorption of NSF_3 [209] lies in the same region as that in the spectrum of SF_6 suggesting all the fluorine atoms to be equivalent and bound to the sulfur atom. The molecule has, therefore, C_{3v} symmetry. This symmetry is further confirmed by I.R. spectrum [209,230] which is similar to OPF_3 as regards to the number and the shape of the bands Calculation of the S-N bond strength from the force constants [209,230,231] $f_{NS}(NSF_3)$ (12.4 mdyne/A^{o}) and f_{SF}(5.6 mdyne/A^{o}) give the bond order of N S; 2.7. These results were confirmed by the microwave spectrum of NSF_3 [232]. It has a dipole moment of 1.91 Debye. The very short S-N bond distance indicates considerable amount of $p\pi(N)-d\pi(S)$ overlap (bond order 2.7). The electronic spectra of NSF_3 has been discussed [231].

Thionitrosyl chloride

The preparation of thionitrosyl chloride can be effected by any one of the following methods.

(a) By the action of chlorine on gaseous thionitrosylfluoride

$$2NSF + Cl_2 \longrightarrow 2NSCl + F_2 \qquad (52)$$

(b) By the action of S_2Cl_2 with ammonium chloride

(c) By thermal fisson of $S_3N_2Cl_2$.

(d) By the action of chlorine upon $S_3N_2Cl_2$ 233,234 .

$$S_3N_2Cl_2 + Cl_2 \longrightarrow 2NSCl + SCl_2 \qquad (53)$$

(e) By reacting S_2Cl_2 vapour and active nitrogen 233

$$S_2Cl_2 + N_2^* \longrightarrow 2NSCl \qquad (54)$$

(f) By the thermal decomposition of trithiazyltrifluoride $N_3S_3Cl_3$ 235,236,237 .

$$N_3S_3Cl_3 \rightleftharpoons 3NSCl \qquad (55)$$

(g) By chlorination of tetrasulfurtetranitride [238]

$$S_4N_4 + Cl_2 \rightleftharpoons N_4S_4Cl_2 \qquad (56)$$

$$N_4S_4Cl_2 + Cl_2 \rightleftharpoons N_3S_3Cl_3 + NSCl \qquad (57)$$

(h) By the reaction of thionylchloride with thionylimide [239]

$$NSOH + OSCl_2 \longrightarrow NSCl + SO_2 + HCl \qquad (58)$$

(i) By the reaction of H_2NS with trithiazyltrichloride [240]

$$H_2NS + N_3S_3Cl_3 \xrightarrow[-HCl]{} NSCl + \tfrac{1}{2} N_4S_4 \qquad (59)$$

Properties

Thionitrosyl chloride, a greenish yellow gas, readily polymerizes to form a stable trimer [236,241,242] .

$$3NSCl \rightleftharpoons N_3S_3Cl_3 \qquad (60)$$

It is moisture sensitive and readily hydrolysed by water to form HNSO, NH_4^+ and SO_3^{--} [239]

$$NSCl + H_2O \longrightarrow HNSO + HCl \qquad (61)$$

$$HNSO + 2H_2O \longrightarrow NH_4^+ + SO_3^{--} \qquad (62)$$

The values of the entholpy and entropy change in the formation of NSCl from trithiazyltrichloride are $\Delta H = 21.9 \pm 3.0$ kcal/mole and $\Delta S^o(NSCl) = 77.5 \pm 9.4$ cal/deg/mole respectively. NSCl is known to react with S_2Cl_2 [233] according to the equation

$$2NSCl + S_2Cl_2 \longrightarrow S_3N_2Cl^+ \; Cl^- + SCl_2 \; .$$

The absolute entropy of NSCl(g) has been calculated from spectroscopic data [243] as 63.66 cal deg^{-1} $mole^{-1}$.

The pressure of NSCl vapour in equilibrium with solid $N_3S_3Cl_3$ is measured in a static system at 31^o to 60^oC [244]. A plot of log P_{NSCl} vs $\frac{1}{T}$ gives a straight line (Fig.VII) through the points corresponds to the equation $P_{NSCl} = 12.321 - \frac{3360}{T}$. From this $H_f(NSCl) = 46.2 \pm 1.5$ kcal/mole and $S(NSCl) = 129.6 \pm 4.8$ cal deg^{-1} $mole^{-1}$ were calculated for the reactions

$$S_3N_3Cl_3(S) \longrightarrow 3NSCl(g)$$

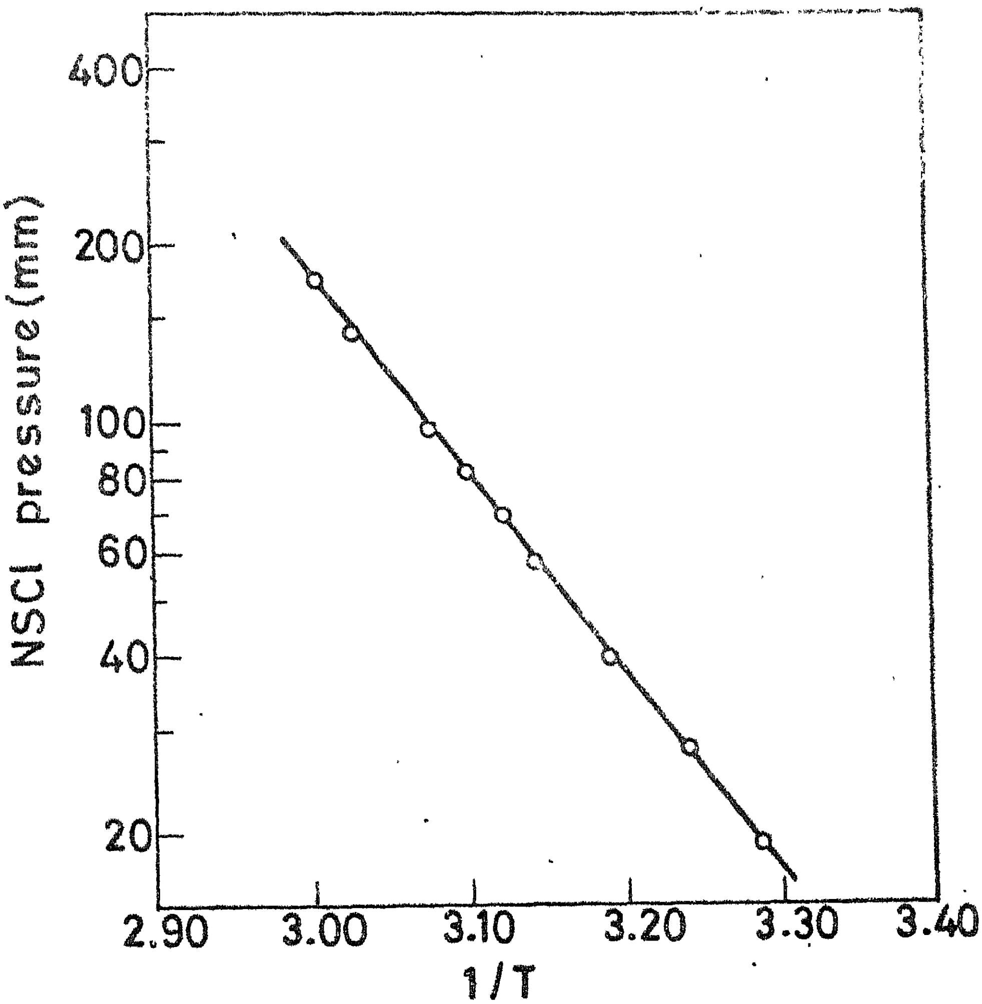


Fig. VII Plot of log P_{NSCl} vs. 1/T.

The i.r. spectrum of NSCl [36,245-247] shows absorption bands due to $\nu_{(NS)}$, $\nu_{(SCl)}$ and $\delta_{(NSCl)}$ at 1320 cm^{-1}, 412 cm^{-1}, 269 cm^{-1} respectively.

Structure

NSCl should be non linear according to Walsh rule 248 with C_s point group. Accordingly its i.r or Raman spectrum shows three allowed bands. From the positions of these bands (1320, 412 and 269 cm^{-1}), force constant were calculated by neglecting the cross terms in the potential function (Table VI). Because of the very high force constant, (f_{NS}=10.02 mdyne/A^{O}) [249] and bond order (NS_1=2.3) values structures (I) and valence bond structures II & III and not the SNCl are proposed for thionitrosylchloride [247].

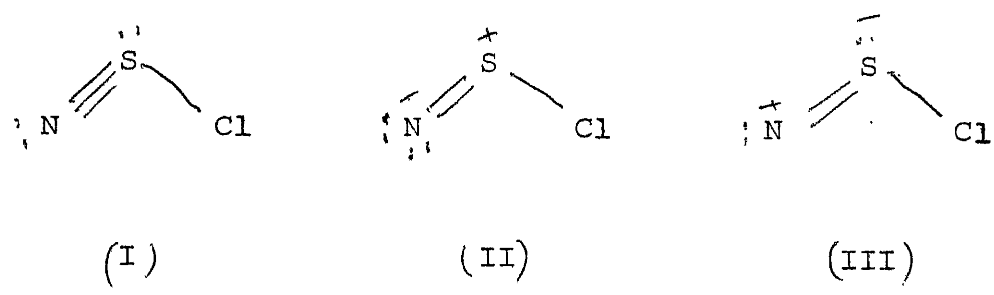


Fig. VII

Table VI. Vibrational frequencies (in cm^{-1}) and force constants (m dyne/Å) for NSCl

Vibration	Frequency	Fundamentals	Force constants
ν_{NS}	1333.0(R) 1323.8(Q) 1316.0(P)	1324.5	10.04 ± 0.07 (F_{11})
ν_{SCl}	423.9(R) 414.4(Q) 405.6(P)	414.8	1.49 ± 0.23 (F_{22})
ν_{NSCl}	281.5(R) 275.2(Q) 261.7(P)	271.6	0.83 ± 0.02 (F_{33})

These structure are similar to those of thionitrosylfluoride. The structures of thionitrosylhalides are different from those of nitrosyl halides, NOX where halide atom is attached to the nitrogen atom and not with the oxygen [250-256]. Microwave spectra [257] of the NSCl was observed by pumping the products of thermally decomposing $N_3S_3Cl_3$ continuously through the cell. The rotation constants were obtained for $N^{14}S^{32}Cl^{35}$, N^{14},$S^{32}Cl^{37}$, and $N^{15}S^{32}Cl^{35}$ in ground vibrational state and from there the molecular dimensions were determined. These are summarized in Table VII.

Table VII. Molecular diamension of NSCl

Compound	$N^{14}S^{34}Cl^{35}$	$N^{14}S^{32}Cl^{37}$	$N^{15}S^{32}Cl^{35}$
r_{NS}	1.450	1.458	1.448
r_{SCl}	2.163	2.157	2.164
$\angle NSCl$	117°,48'	118°,8'	117°,45'

The S-Cl bond length of NSCl is longer than the sum of Pauling's covalent radii (1.04 + 0.99 = 2.03 A°). This anomaly in the bond length seems consistent with the fact

that the quadrupole coupling constant of the Cl nucleus is smaller than the average value for many ordinary molecules. This indicates the ionic weak nature of S-Cl bond in the thionitrosyl molecule.

Structural Correlations

Various attampts have been made to establish a relationship between the N-S bond distance (r_{NS}) and the bond order. η_{NS} (Fig. X) in order to characterize the N-S bond in NSF, NSF_3 and NSCl. As a result of this a relationship between r_{NS} and f_{NS} has been found which takes the form $f_{NS} = 145.\ r_{NS}^{-7.00}$. However this linear dependence of r_{NS} and η_{NS} [14,124,258,259] shall be considered only as an approximation. The Table VIII shows physical properties and Table IX shows force constants, bond distances, band orders bond energies and i.r. frequencies for NSF, NSF_3 and NSCl. The frequency observed for NSF($1372 cm^{-1}$) suggests that its bond order is less than that in NSF_3($1515 cm^{-1}$) and greater than that in NSCl ($1320\ cm^{-1}$) (Fig. IX).

Table VIII. Physical Properties of NSF, NSF_3 and NSCl

Compound	NSF	NSF_3	NSCl
Molecular weight	65.01	103.01	81.46
Colour	pale yellow	colourless	greenish yellow
M.P.	-89	-72.6 ± 0.5	-
B.P.	$+0.4\pm2.0$	-27.1 ± 0.1	-
Density	-	1.92	-
Molar heat of volatilisation (cal)	6052 ± 30	5526 ± 50	-
Enthalpy of formation Hf	41 ± 2 kcl/mole	-85 kcal/mole	21.9 ± 3.0 kcl/mole
Trouton's constant	22.1	22.5	-

Table IX. Force Constant, Bond distance, Bond order and I.R. frequencies for NSF, NSF_3 and NSCl

Compound	η_{NS} (A^{o})	f_{NS} (mdyne/A^{o})	η_{NS}	Bond energy d_{NS}	I.R.** (cm^{-1})
NSF	1.446	10.71	2.4	71	1372 640 366
NSF_3	1.416	12.55	2.7	93	1515 (ν_{NS}) 811 ν_{SF} 775
NSCl	1.46	10.02	2.2	-	1320 412 273

** The frequencies are written in order ν_{NS}, ν_{SX} and δ_{NSX}

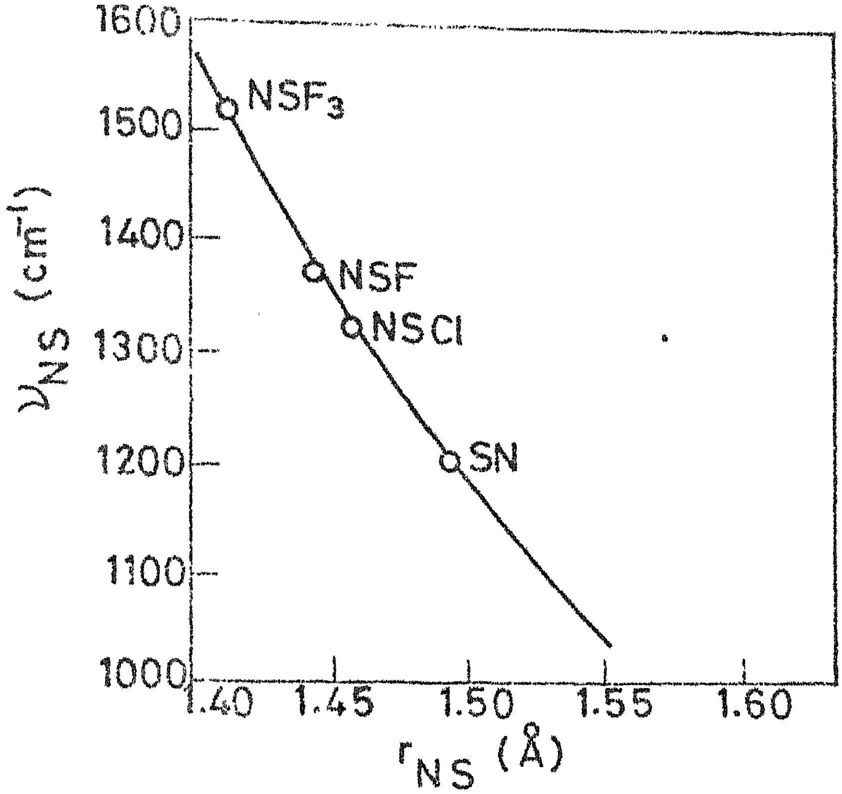


Fig. IX Correlation of S-N stretching frequencies and bond lengths.

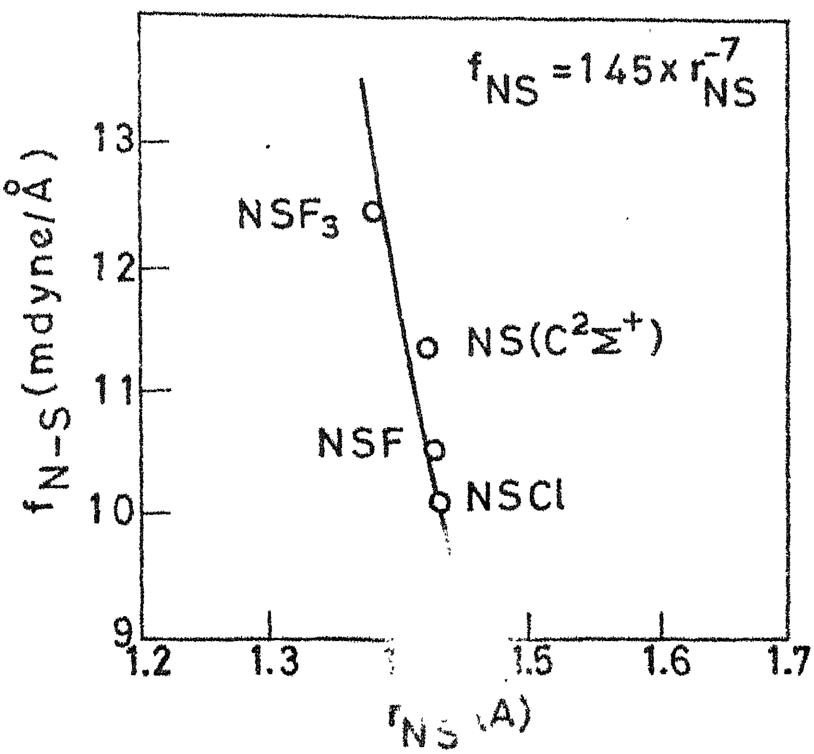
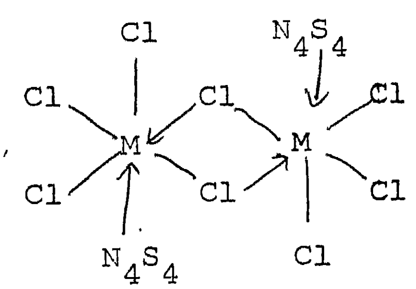


Fig. X Correlation of force constants and band lengths.

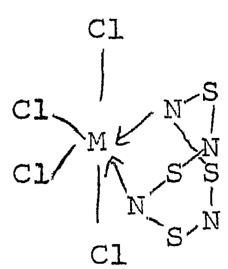
Metallic and Non Metallic Adducts and Compounds of Sulfur Nitride

Many reactions of S_4N_4 or S_2N_2 with the compounds of the transition metals, post transition metals and with Lewis acids give rise to compounds in which (i) there are S-N ligands or (ii) there are adducts molecule of S_4N_4. These have been well reviewed [1,6] and only the main results will be described here (Table X).

Two type of structures have been found for S_4N_4 adducts complexes. X-ray structure determination of $S_4N_4SbCl_5$ [260] and $S_4N_4BF_3$ [261] show that in the solid state they are covalent with donor nitrogen and unidentate S_4N_4. Conductance measurements have established [262] that in solution some compounds are ionized. Several other structures are possible in the solid state and in solution, for instances, (I) [263], (II) [260] and especially for 'soft' Lewis acids, structures which include donor sulfur.



(I)



(II)

Fig. XI

Table X. Compounds of S_4N_4 and S_2N_2 and their melting point and colour

S.No.	Compound	Colour(m.p.)	References
1	$S_4N_4TiCl_4$	(RBr,132)	264, 265, 266
2	$S_4N_42TiCl_4$	(RBr, -)	264 - 266
3	$S_4N_4TiBr_4$	(DBr, 138)	264, 267
4	$S_4N_4TiF_4$	(O, 120)	267
5	$S_4N_4TiI_4$	(B, 100)	267
6	$S_4N_4VCl_4$	(Br, 190)	263, 264
7	$S_4N_42FeCl_3$	(RBr, 80)	267
8	$Fe(NS)_4$	(B, -)	268, 271, 272
9	$Co(NS)_4$	(DV, -)	269, 271, 272
10	$Ni(NS)_4$	(DV, -)	270, 271, 272
11	$Cu(NS)_2$	(Br, -)	273
12	$(CuNS)_4$	(B, -)	273
13	$Cu(NS)_2Cl_2$	(B, -)	273
14	S_4N_4CuCl	(B, -)	274
15	S_4N_4CuBr	(B, -)	274
16	$S_4N_4CuCl_2$	(B, -)	274
17	$S_4N_4ZrCl_4$	(RO, 260)	264, 267
18	$S_4N_4NbCl_5$	GBr, 180)	264
19	$S_4N_4MoCl_5$	(Bl, -)	260, 275
20	$Ag(NS)_2$	(RBr, -)	273
21	$S_4N_4HfCl_4$	(R, 140)	267

22	$S_4N_4TaCl_5$	(R, 180)	264, 267
23	$S_4N_4WCl_4$	(Br, –)	274, 267
24	$S_4N_4WBr_4$	(DaBr, 251)	267
25	$S_4N_4WOCl_4$	(DaBr, –)	267
26	$Pt(N_4S_4)(PPh_3)_2$		276
27	$Pt(N_2S_2)(PPh_3)_2$		276
28	$Pt(NS)_4$	(DaBr, 144)	272
29	$Pt(N_2S_4)(PPh_3)_2$		276
30	$Hg(SN)_2$		277, 278
31	$Hg(SN)_2$		277, 278
32	$S_4N_4BF_3$	(DaR, 145-147)	279, 280
33	$S_4N_4BCl_3$	(OR, 138)	262, 264, 280
34	$S_4N_4 2BCl_3$	(OBr, –)	262, 264, 280
35	$S_4N_4BBr_3$		280
36	$S_4N_4AlCl_3$	(DaR, –)	281
37	$S_4N_4AlBr_3$	(O, 122°C)	281
38	$S_4N_4 2AlBr_3$	(OBr, 144)	265
39	$S_4N_4 2GaCl_3$	(DR, 100)	267
40	$S_4N_4 2InCl_3$	(RBr, 100)	267
41	$S_4N_4\frac{1}{2}SnCl_4$	(DR, 200-202)	264, 275
42	$S_4N_4\frac{1}{2}SnBr_4$	(DBr, 198-200)	282, 283
43	$S_4N_4 2SbF_5$		284, 285
44	$S_4N_4 4SbF_5$	(g, 145)	284, 285
45	$S_4N_4SbCl_5$	(DR, 160-162)	262, 264, 275
46	$S_4N_4 2SbCl_5$		262, 264, 275

47	$S_4N_42SbBr_3$		284
48	$S_4N_42SbI_3$		284
49	$S_4N_4SO_3$		286, 287
50	$S_4N_42SO_3$		286, 287
51	$S_4N_44SO_3$		286, 287
52	$S_4N_4SeCl_4$	(Y,127-129)	262
53	$S_4N_4Se_2Cl_2$	(Y, -)	265
54	$S_4N_4SeCl_4SO_3$		264
55	$S_4N_4TeCl_4$	(DR, 140^{o}C)	262
56	$S_4N_4TeB_4$		288
57	$S_4N_4TeCl_4BCl_3$		264
58	$S_4N_4TeCl_4SbCl_5$		264
59	$S_4N_4TeCl_4SO_3$		264
60	$S_4N_4SnCl_4POCl_3$		289
61	$S_3N_2CF_3CON$	(Y, -)	290
62	$S_3N_4AsPh_3$		291

witnin brackets the letters indicate the following colours and the numbers for melting point in ^{o}C.

B= black; Bl= blue; Br= brown; D= deep; Da= dark;
Y= green; O= orange; R= red, V= violet; Y=yellow.

The chemistry of the $N_2S_2^+$ [292], $S_3N_3^-$ [293-296], $S_4N_3^+$ [297-311], $S_4N_4^-$ [123, 311-313], $S_4N_5^-$ [295, 296, 314, 315], $(S_5N_5)^+$ [311, 316, 317] and $S_5N_6^-$ [315] have also been studied.

Transition Metal thionitrosyl complexes

Recently, there has been a considerable upsurge in the study of transition metal thionitrosyl complexes. This is partialy due to the increase in understanding of the way in which NS binds to a metal. Similar to nitrosyl complexes, there are three principal bonding modes in thionitrosyl complexes: (a) terminal, linear M-N-S groups (b) terminal, bent M-N-S groups and (c) bridging NS groups. In case (a) the thionitrosyl ligand can be represented as coordinated "NS^+" and in (b), as coordinated "NS^-".

It is convenient to classify MNS complexes by the number of d type electrons present in the complex. Thus, MNS complex with n number of d electrons of M plus the number of electrons in the π^* orbitals of NS (or more conveniently, n is the number of d electrons if the thionitrosyl is regarded as being coordinated as NS^+) would be written as $\{MNS\}^n$. This classification scheme will be used throughout the remainder of this review.

Seven Coordination

The compounds $[Mo(NS)(S_2CNR_2)_3]$, (R_2=Me_2, Et_2, $(CH_2)_4$) have been shown to be seven coordinated [318, 319]. These were prepared by treating dioxo complex, $MoO_2(S_2CNR_2)_2$ with

trimethylsilylazide in acetonitrile under reflux. It seemed likely that this reaction proceeds via intermediate formation of a nitrido complex and subsequently the nitrido complex $[MoN(S_2CNR_2)_3]$ reacts with elemental sulfur in refluxing acetonitrile to give the thionitrosyl complexes.

$$MoN(S_2CNR_2)_3 \quad + \quad S_8 \xrightarrow[\text{reflux}]{CH_3CN} Mo(NS)(S_2CNR_2)_3$$

(yield could be improved by using propylene sulphide).

These complexes are yellow, stable in air, diamagnetic and nonconducting in 1,2-dichloroethane solution. The 'H nmr spectrum of $[Mo(NS)(S_2CNMe_2)_3]$ in nitrobenzene at room temperature shows a 1:2:3 triplet due to the dithiocarbonate methyl group. The structure of $[Mo(NS)(S_2CNMe_2)_3]$ has been described as pentagonal bipyramide with the thionitrosyl group in one of the apical positions. The M-N-S angle for this MNS^{4} complex is 172.0(7) [320]. The structure is shown schematically in Fig. XII.

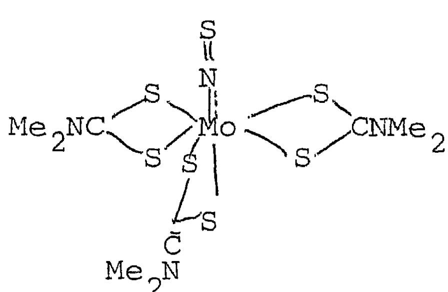


Fig XII

In the thionitrosyl complex the Mo-N bond length (1.74A^{o}) is longer than in the nitride (1.64A^{o}), as would be expected specially, if the thionitrosyl ligand behaves in a manner analogous to the NO^{+} ligand, as the almost linear Mo-N-S system implies. A comparision between thionitrosyl complex and the analogous molecule [$Mo(NO)(S_2CNBu^n_2)_3$] [321] is summarized in Table XI.

TABLE XI

Complex	Mo-N distance	M-N-X
$Mo(NS)(S_2CNMe_2)_3$	1.73A^{o}	173.2^{o}
$Mo(NO)(S_2CNBu^n_2)_3$	1.74A^{o}	172.0(7)

The Mo-N bond distance and M-N-X angle are equal, within the limit of experimental error. Thus it would seem that the NS and NO ligands are quite similar. The N-S distance in the free NS ligand [322] or the value calculated from the sums of covalent radii for an N=S double bond or even values found in a variety of compounds purporting to contain N=S partially multiple bonds [323] is smaller than the N-S distance (1.59A^{o}) in the [$Mo(NS)(S_2CNMe_2)_3$] which is consistent with a considerable degree of M— NS π back bonding.

The thionitrosyl sulfur in these complexes can be alkylated with triphenylmethyl tetrafluoroborate to give $[Mo(NSCP_3)(S_2CNR_2)_3]BF_4$ [319,325] .

Six Coordination

All six coordinate complexes so far prepared are thio- mononitrosyls.

Ruthenium Complexes

Only two thionitrosyl complexes of ruthenium, (one with triphenylphosphine and one with triphenylarsine), are so far known which were prepared by the reaction of $RuCl_3 \cdot XH_2O$ with $(NSCl)_3$ in THF or in CCl_4-$CHCl_3$ mixture in the presence of triphenylphosphine and triphenylarsine 325 . (In THF or in $CHCl_3$-CCl_4 mixture, the trithiazyltrichloride probably act as a solvated monomer).

$$RuCl_3XH_2O \;+\; \tfrac{1}{3}(NSCl)_3 L \xrightarrow{THF} Ru(NS)Cl_3L_2 \qquad (63)$$

$$(L = PPh_3 \text{ or } AsPh_3)$$

The i.r. spectra showed a strong sharp absorption bands in the 1290-1295 cm^{-1} region assigned to ν_{NS}. The complexes are air stable, non conducting in nitrobenzene and are

diamagnetic. The structure of $Ru(NS)Cl_3(AsPh_3)_2$ has been determined by X-ray crystallography [326]. Full details of structure have not yet been published. The Ru-N-S angle is 179^o suggesting that the NS ligand is functioning as a three electron donor. Thus, these six coordinate $(RuNS)^6$ complexes have been regarded as complexes between Ru(II) and NS^+. The metal ligand bond was considered, by analogy with the NO^+, to be formed by donation of electrons from nitrogen to the metal and back donation from the filled metal d-orbitals to π^*(NS) orbitals.

Rhodium Complexes

Six coordinate complexes of the type $Rh(CO)(NS)Cl_2L_2$ ($L=PPh_3$ or $AsPh_3$) have recently been reported [327,328]. Trithiatrichloride reacts with trans $Rh(CO)ClL_2$ in tetrahydrofuran to produce the diamagnetic, nonelectrolyte, $Rh(CO)(NS)Cl_2L_2$ complexes.

$$\text{Trans } Rh(CO)ClL_2 + \tfrac{1}{3}(NSCl)_3 \xrightarrow{THF} Rh(CO)(NS)Cl_2L_2$$

The reaction of $RhH(CO)(PPh_3)_3$ with $(NSCl)_3$ in carbon tetrachloride-chloroform mixture gives a deep green chloro-bridged complex, $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ which on reaction with excess triphenylphosphine or triphenylarsine in

dichloromethane yields yellowish orange complexes $[Rh(CO)(NS)Cl_2L_2]0.5CH_2Cl_2$ L=PPh_3 or $AsPh_3$ as a result of cleavage of chloro bridge. Their infrared spectra showed absorption bands in the range 2100-2110 cm^{-1} (ν_{CO}), 1118-1120 cm^{-1} (ν_{NS}) and 330 cm^{-1} (terminal ν_{Rh-Cl}). In the spectrum of the green complex a band appeared at 260 cm^{-1} which is assigned to bridged ν_{Rh-Cl}. The diamagnetism of complexes indicate the oxidation state of rhodium either +1 or +3. The high ν_{CO} frequency (ν_{CO}, 2100 cm^{-1}) in these complexes as compared to that in original compound (ν_{CO}, 1960 cm^{-1}) suggested +3 oxidation state of the rhodium. The shifting of the ν_{CO} band towards higher wave numbers may possibly be due to the strong σ-bonding trans effect of the trans NS^- group. Thus, these six coordinate, bent, $(RhNS)^8$ complexes have been regarded as complexes between Rh(III) and NS^-. The probable structures of $Rh(CO)(NS)Cl_2(PPh_3)_2$(I) and $Rh(CO)(NS)Cl_2L_2$(II) are

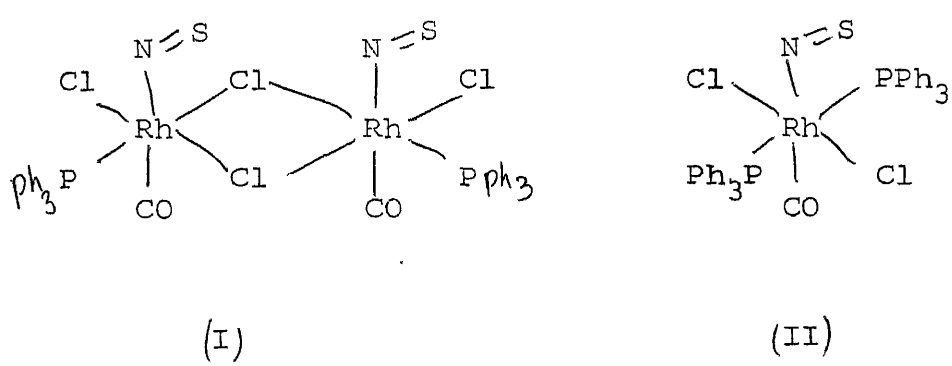


Fig. XIII

The reaction of compounds $Rh(CO)(NS)Cl_2L_2$ with NOCl in CH_2Cl_2 afforded corresponding nitrosyl complexes $Rh(CO)Cl_2L_2$ ($L = PPh_3$ or $AsPh_3$)

Rhenium Complexes

Reactions of S_2Cl_2 with $[ReCl_2(PRPh_2)_2N]$ (R=Ph or Pr^n) give thionitrosyl complexes, $ReCl_3(NS)(PRPh_2)_2$. The complexes $[ReX_2N(PR_3)_3]$, (PR_3 = PMe_2Ph, PEt_2Ph or $PMePh_2$; X=Cl or Br) react with half an equivalent of S_2Cl_2 to give the thionitrosyl $[ReClX(NS)(PR_3)_3]$. Reaction of nitrido complex $[ReCl_2N(PR_3)_3]$ with an excess of S_2Cl_2 or SCl_2 gave the derivatives $[ReCl_3(NS)(PR_3)_2]$. The formation of thionitrosyl from nitrido and S_2Cl_2 is possibly according to the scheme given in equation (64) [319, 329].

$$[ReCl_2N(PR_3)_3] + 0.5S_2Cl_2 \longrightarrow [ReCl_2(NS)(PR_3)_3] + Cl \qquad (64)$$

$[Re(NS)Cl_2(PMe_2Ph)_3]$ reacts with K(CNS) or $Na(S_2CNMe_2)$.

$$[Re(NS)Cl_2(PMe_2Ph)_3] + KCNS — [Re(NS)Cl(NCS)(PMe_2Ph)_3] + KCl \qquad (65)$$

$$[Re(NS)Cl_2(PMe_2Ph)_3] + Na(S_2CNMe_2) \longrightarrow [Re(NS)Cl(PMe_2Ph)_2(S_2CNMe_2)] + NaCl \qquad (66)$$

Reaction of S_2Cl_2 with $[ReCl(N)(dPPe)_2]Cl$ ($dPPe=Ph_2PCH_2CH_2PPh_2$) yields $[Re(NS)Cl(dPPe)_2]Cl$ which reacts with $FeCl_3$ or NH_4PF_6 to give $FeCl_4^-$ or PF_6^- salts according to equations

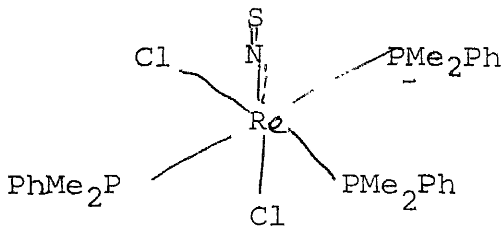
$$[Re(NS)Cl(dPPe)_2]Cl + FeCl_3 \longrightarrow [Re(NS)Cl(dPPe)_2]^+[FeCl_4]^- \quad (67)$$

$$[Re(NS)Cl(dPPe)_2]Cl + NH_4PF_6 \longrightarrow [Re(NS)Cl(dPPe)_2]^+[PF_6]^- + NH_4^+ + Cl^-$$

The salt $[Re(NS)Cl(dPPe)_2](S_2CNEt_2)$ is prepared by the reaction of $[ReCl(N)(dPPe)_2]Cl$ and $Na(S_2CNEt_2)$.
$Re(NS)Cl(dPPe)_2L$ ($L= Cl, FeCl_4$ or PF_6) are yellow and have conductivities in nitrobenzene typical of 1:1 electrolytes. In the infrared, a single strong peak observed in the region 1167-1185 cm^{-1} confirms the presence of the NS^+ group in these compounds.

The hydrogen -1 n.m.r. spectrum of $[ReNSCl_2(PMe_2Ph)_3]$ shows two triplets and a doublet in the tertiary phosphine alkyl group region, indicating a meridional configuration for the phosphine ligands with the NS group trans to Cl. An x-ray crystal structure analysis of the analogous nitrosyl complex $[Re(NO)Cl_2(PMe_2Ph)_3]$ shows the M-N-O system to be essentially linear with Re-N-O 178.8 (1.4)$^\circ$ [330]. It is

therefore extremely likely that the thionitrosyl analogoues are isostructural with linear NS groups.



(II)

Fig. XIV

The H n.m.r. spectrum of [$Re(NS)Cl(S_2CNMe_2)(PMe_2Ph)$] shows a singlet in the dithiocarbamate methyl region and a pair of doublets in the tertiary phosphin alkyl group region, indicating configuration(III).

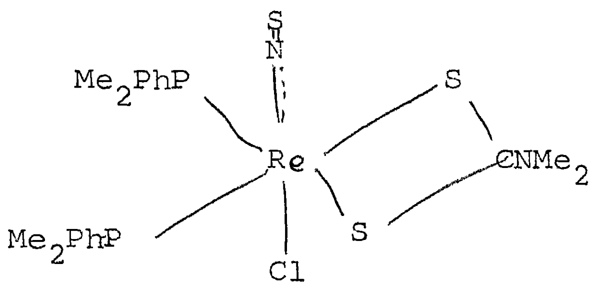


Fig. XV (III)

The complexes, [$Re(NS)Cl_3(PR_3)_2$] are paramagnetic with magnetic moments in the range 1.84-2.01 B.M. These values are close to that found for the analogous complex [$Re(NO)Cl_3(PMe_2Ph)_2$] .

Osmium Complexes

Green complexes of osmium have been reported as a result of reactions of OsX_3NL_2 ($L=AsPh_3$, PMe_2Ph) or $\frac{1}{2}$ bipy (2.2' bipyridyl) with half an equivalent of S_2Cl_2. Addition of pyridine (P_y) to a methylene chloride solution of the product formed by reaction of salt $(NBu_4)[OsCl_4N]$ with S_2Cl_2, gives green $[Os(NS)Cl_3(P_y)_2]$ [319] . The osmium thionitrosyl complexes, $[Os(NS)Cl_3L_2]$ ($L=PPh_3$ or $AsPh_3$) were prepared by the action of trithiazyltrichloride in THF with osmium trichloride in presence of triphenylphosphine or triphenylarsine respectively [325]

$$OsCl_3 + 2L \xrightarrow{(NSCl)(THF)_x} Os(NS)Cl_3L_2 \qquad (68)$$

$$L = PPh_3 \text{ or } AsPh_3$$

These complexes are diamagnetic and non electrolyte. In their infrared spectrum, a strong band is observed in the range 1270-1282 cm^{-1} indicating that the thionitrosyl group is coordinated as NS^+. The ^1H n.m.r. spectrum of $[Os(NS)Cl_3(PMe_2Ph)_2]$ shows a triplet due to the tertiaryphosphine methyl groups. This is consistent with the Fig. XVI with trans virtually coupled phosphorus ligands.

TABLE XII. Six Coordinate thionitrosyl complexes

Compound	Colour	N-S stretching frequencies cm^{-1}	Refs.
$Ru(NS)Cl_3(PPh_3)_2$	red brown	1290	325
$Ru(NS)Cl_3(AsPh_3)_2$	red brown	1295	325, 326
$Rh(CO)(NS)Cl_2PPh_3\ _2$	green	1118	327
$Rh(CO)(NS)Cl_2(PPh_3)_2 0.5CH_2Cl_2$	orange red	1120	327, 328
$Rh(CO)(NS)Cl_2(AsPh_3)_2 0.5CH_2Cl_2$	orange red	1120	328
$Re(NS)Cl_2(PMe_2Ph)_3$	pink	1180	319
$Re(NS)Cl_2(PEt_2Ph)_3$	pink	1167	319
$Re(NS)Cl_2(PMePh_3)_3$	pink	1172	319
$Re(NS)ClBr(PEt_2Ph)_3$	pink	1168	319
$Re(NS)Cl(SCN)(PMe_2Ph)_3$	red pink	1177	319
$Re(NS)Cl(S_2CNMe_2)(PMe_2Ph)_2$	yellow brown	1150	319
$[Re(NS)Cl(dppe)_2]Cl$	yellow	1185	319
$[Re(NS)Cl(dppe)_2]PF_6$	yellow	1177	319
$[Re(NS)Cl(dppe)_2]FeCl_4$	yellow	1173	319
$[Re(NS)Cl(dppe)_2]S_2CNEt_2$	yellow	1183	319
$[Re(NS)Cl_3(PMe_2Ph)_2]$	purple	1228	319
$[Re(NS)Cl_3(PEt_2Ph)_2]$	purple	1230	319
$Re(NS)Cl_3(PMePh_2)_2$	purple	1220	319
$Re(NS)Cl_3(PPh_3)_2$	purple	1214	319

$Re(NS)Cl_3(PPr^nPh_2)_2$	purple	1226	319
$Os(NS)Cl_3(PPh_3)_2$	green	1285	325
$Os(NS)Cl_3(AsPh_3)_2$	green	1282	319,325
$Os(NS)Cl_3(PMe_2Ph)_2$	green	1285	319
$Os(NS)Cl_3(bipy)$	green	1282	319
$Os(NS)Cl_3(P_4)_2$	yellow green	1284	319
$Os(NS)ClBr_2(AsPh_3)_2$	green	1270	319
$Os(NS)ClBr_2(bipy)$	green	1280	319
$Ir(CO)(NS)Cl_2(PPh_3)_2$	orange	1120	331

that the Vaska's complex in solution takes up oxygen from the atmosphere to form oxygen complex which on reaction with $(NSCl)_3$ forms thionitritoiridium complex.

Five Coordination

These thionitrosyl complexes are amongst the very few examples of five coordination they are thionitrosyl derivatives of rhodium triphenylphosphine of general formula $Rh(NS)ClX(PPh_3)_2$ (X= Cl, Br) [332]. They are prepared by the reaction of $RhX(PPh_3)_3$ with trithiazylchloride in THF as red brown amorphous solid which are diamagnetic and nonconducting in nitrobenzene. $Rh(NS)Cl_2(PPh_3)_2$ is also prepared by action of $Rh(NS)(PPh_3)_3$ with chlorine gas [331] . The i.r. spectra of these complexes showed a absorption band in the region 1117-1120 cm^{-1} which was assigned to ν_{NS}. By analogy with nitrosyl complex $Rh(NO)Cl_2(PPh_3)_2$ the thionitrosyl complex $Rh(NS)Cl_2(PPh_3)_2$ may have the structure.

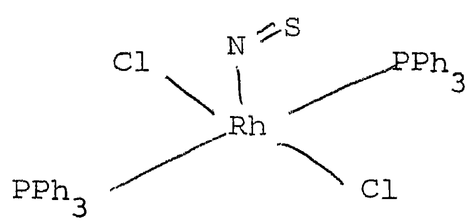


Fig. XVII

They are covalent in nature and soluble in benzene, chloroform and dichloromethane.

<u>Four Coordination</u>

There are two compounds in this class, one each of chromium and rhodium. The action of trithiazyltrichloride on Na $[\eta^5\text{-}C_5H_5Cr(CO)_3]$ in tetrahydrofuran gave di-carbony (η^5 cyclopentadinyl) thinitrosylchromium(I) $\eta^5\text{-}C_5H_5Cr(CO)_2(NS)$ as dark red violet, diamagnetic solid [333-335]

$$\mathrm{Na}\ [\eta^5\text{-}(C_5H_5)Cr(CO)_3] + \tfrac{1}{3}(NSCl)_3 \xrightarrow{THF} [\eta^5\text{-}C_5H_5Cr(CO)_2NS] + CO + NaCl \quad (69)$$

Its i.r. spectrum shows three strong bands attributable to terminal CO and NS groups.

The structure of $[\eta^5\text{-}(C_5H_5)\ Cr(CO)_2NS]$ has been determined by x-ray crystallography [334,335] and is shown schematically in (Fig.XVI). Its molecular geometry is similar to that exhibited by molecules $[\eta^5\text{-}C_5H_5Mn(CO)_3]$ [336] and $[\eta^5\text{-}C_5H_5Cr(CO)_2NO)]$ 338 and the Cr-C (cp), Cr-C (O) and C-O bond lengths are comparable to those found in other cyclopentadienyl cromium carbonyls [337] . The Cr-N-S angle is 176.8(2) (Table XIII) suggesting that the thionitrosyl ligand coordinates essentially linearly to the metal via the nitrogen atom. Hence the thionitrosyl group can be considered to be bonded as NS^+, a mode of coordination that is directly analogous to metal-thiocarbonyl bonding

A comparison of the spectroscopic properties of the compounds $(\eta^5\text{-}C_5H_5)Cr(CO)NX(X=O,S)$, suggests that the NS ligand is more effective in removing electron density from the central atom than is the NO ligand.

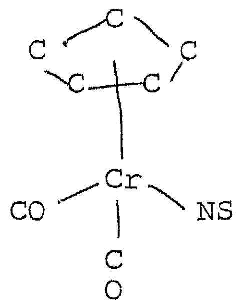


Fig. XVIII

The reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ with NOCl and $NOPF_6$ gave the nitrosyl complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ and a water sensitive, green black solid $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)]PF_6^-$.

The rhodium thionitrosyl $Rh(NS)(PPh_3)_3$ is prepared by action of trithiazyltrichloride in THF with hydrated rhodiumtrichloride in the presence of excess of triphenylphosphine and granulated zinc [331]

$$RhCl_3 3H_2O + 3PPh_3 \xrightarrow[\text{THF, } 60^\circ C]{\text{Zn, }(NSCl)_3} Rh(NS)(PPh_3)_3 \qquad (70)$$

Table XIII. Four Coordinate Thionitrosyl Complexes

Complex	Colour	m.p. (^{o}C)	I.R. frequencies ν_{CO} (cm^{-1})	ν_{NS} (cm^{-1})	$\nu_{(NO)}$ (cm^{-1})
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$	Red violet	68-69	2033,1962	1180	-
$(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)\ PF_6$	Green black	-	2122	1243	1790
$Rh(NS)(PPh_3)_3$	Pink	155	-	1120	-

TABLE XIV. Crystallographic Data on (η^5-C_5H_5)-Cr(CO)$_2$NS

Bonds and angles	Values A or degrees
Cr-N	1.694(3)
Cr-C(O)	1.883(3)
C-O	1.131(3)
N-S	1.551(3)
$\angle$Cr-N-S	176.8 (2)
$\angle$Cr-C-O	178.1 (2)
$\angle$C(O)-Cr-C(O)	92.4 (2)
$\angle$C(O)-Cr-N	94.8 (1)

Reaction of $Rh(NS)(PPh_3)_3$ with chlorine gas afforded a reddish brown compound $Rh(NS)Cl_2(PPh_3)_2$

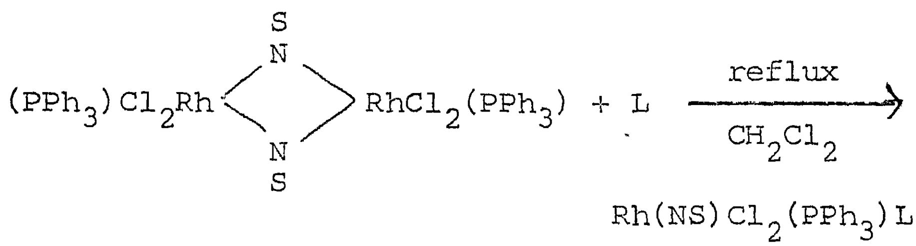
$$Rh(NS)(PPh_3)_3 + Cl_2 \longrightarrow Rh(NS)Cl_2(PPh_3)_2 + PPh_3$$

It is pink coloured, diamagnetic and nonconducting crystals. Its i.r. spectrum showed a strong absorption band at 1120 cm^{-1} which is assigned to ν_{NS}.

Bridged thionitrosyl complex

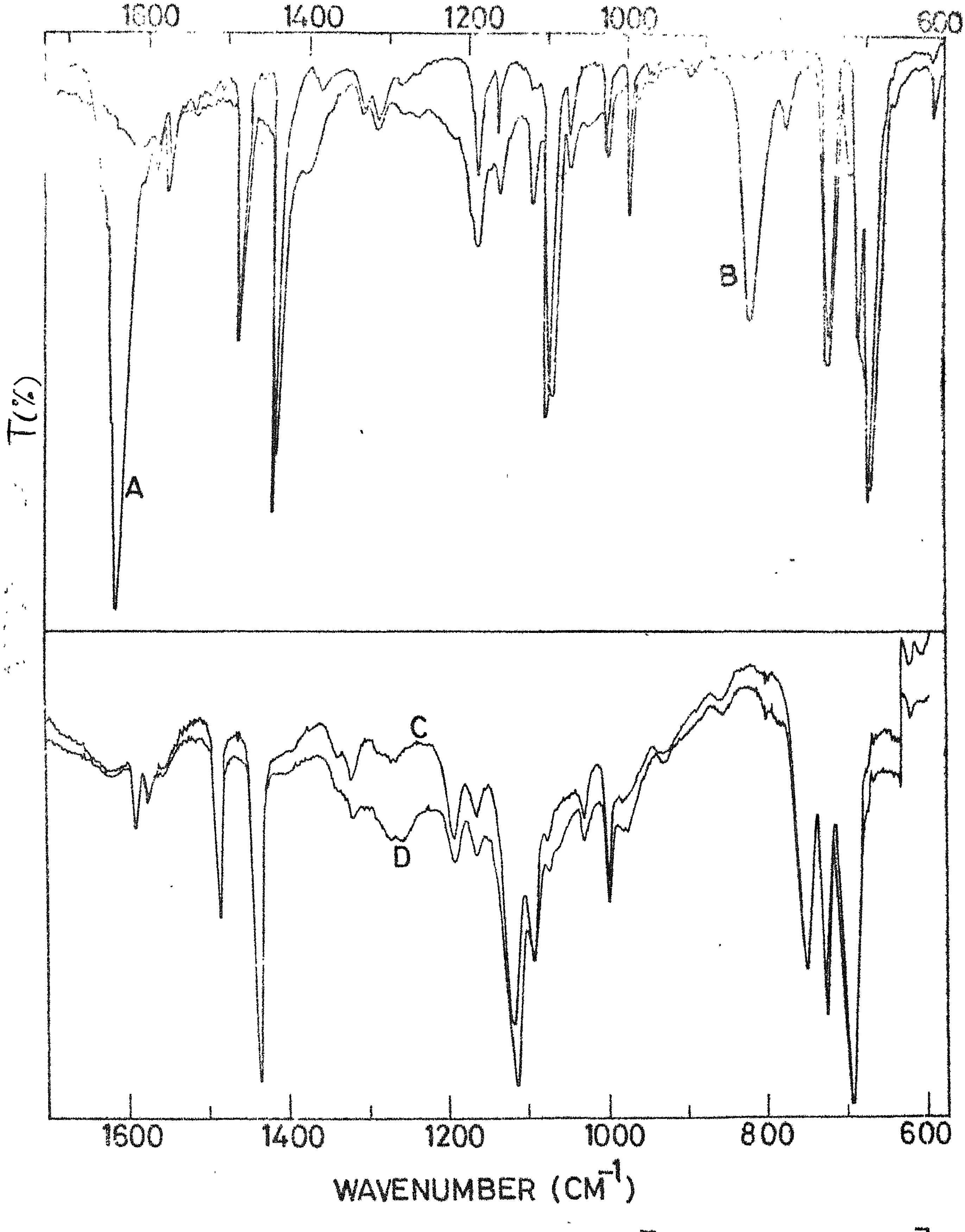
The reaction of a carbontetrachloride solution of $(NSCl)_3$ with $Rh(NO)Cl_2(PPh_3)_2$ in $CHCl_3$ under argon atmosphere produces a thionitrosyl bridged complex $[Rh(NS)Cl_2(PPh_3)]_2$ [338] which is air stable diamagnetic and nonelectrolyte in solution. Its i.r. spectra (Fig. XIX) did not show any band due to $\nu_{(NO)}$ at 1630 cm^{-1} but a new slightly broad band at 840 cm^{-1} appeared which was attributed to the bridging thionitrosyl groups. These results were interpreted as the replacement of NO group in the compound by the NS. The broadening of the 840 cm^{-1} band was suggested to be due to the two NS bands $\nu_{as}(NS)$ and $\nu_{sy}(NS)$ appearing close together. NS bridge in the compound were further

proved by reacting it with PPh_3 and $AsPh_3$ which resulted in the NS bridge cleavage.



($L = PPh_3$ brown m.p. 145°C)
($L = AsPh_3$ red brown m.p. 160°C)

The i.r. spectra of $Rh(NS)Cl_2(PPh_3)L$ ($L=PPh_3$ or $AsPh_3$) showed a characterstic band of terminal NS group at 1120 cm^{-1} which further conforms with the fact that the band at 840 cm^{-1} in complex $[Rh(NS)Cl_2(PPh_3)]_2$ is a characterstic band of bridging thionitrosyl group.



A. $Rh(NO)Cl_2(PPh_3)_2$ B. $[Rh(NS)Cl_2(PPh_3)]_2$

C. $Rh(NS)Cl_2(PPh_3)_2$ D. $Rh(NS)Cl_2(PPh_3)(AsPh_3)$

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Infrared Spectra

Spectra of the compounds were recorded with a Parkin-Elmer 580 Infrared Diffraction Grating Spectrophotometer in the 4000-200 cm^{-1} range. Samples were prepared as KBr and CsI pellets.

Conductivity Measurements

Conductivity measurements of the compounds were made in the Elico conductivity meter type CM-80 of millimolar solutions in nitrobenzene.

Magnetic Susceptibility Measurements

These measurements were made using a Gouy balance at room temperature (30°C).

Melting Points

Melting points of the compounds were recorded on a Fisher-Johns melting point apparatus. The results are recorded in Table II.1.

Results and Discussion

(NSCl) $(solvent)_x$ reacts with $RhH(PPh_3)_4$ to give a brown chlorobridged complex $[Rh(NS)Cl_2(PPh_3)]_2$ (I). The interaction of (I) with triphenylphosphine in CH_2Cl_2 gave

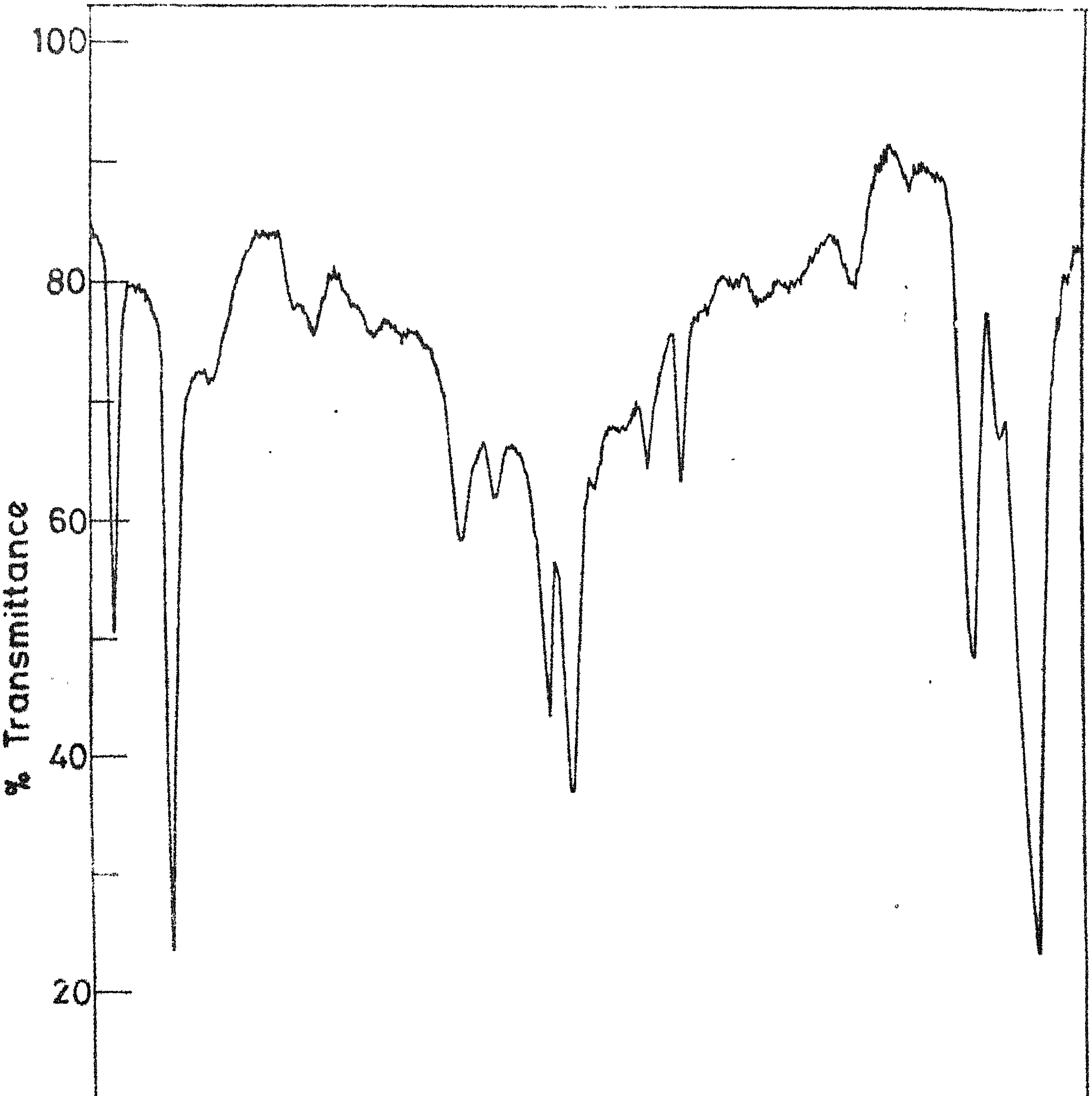

Fig. 1 IR spectrum of $[Rh(NS)Cl_2(PPh_3)]_2$.

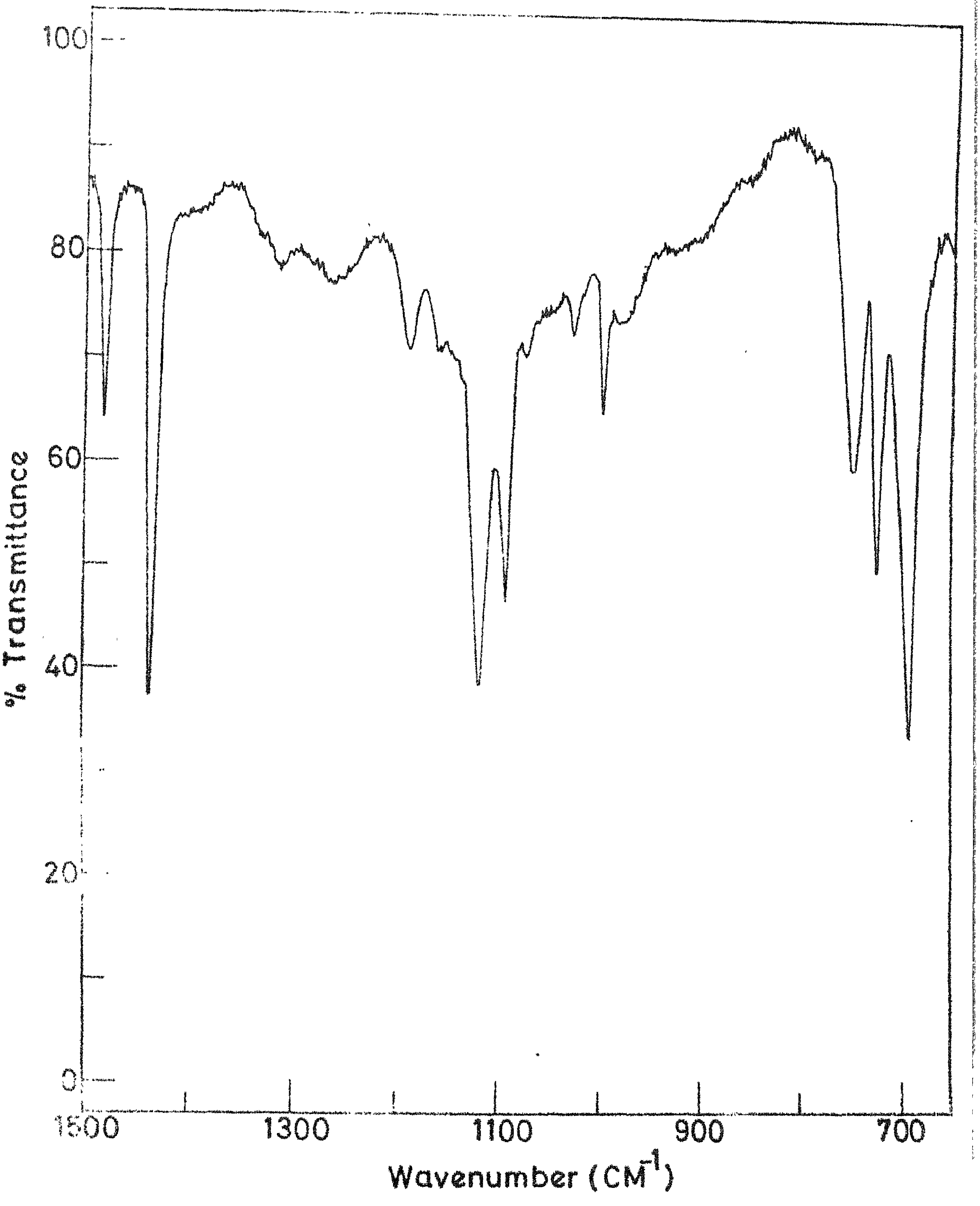

Fig. 2 IR spectrum of $Rh(NS)Cl_2(PPh_3)_2$.

a brown complex, $Rh(NS)Cl_2(PPh_3)_2$(II). The infrared spectra of both the complexes I and II showed absorption bands 1118-1120 cm^{-1} (ν_{NS}) and 330 cm^{-1} (terminal ν_{Rh-Cl}) (Fig. 1 and 2). In the spectrum of I a band appeared at 260 cm^{-1} which was not present in II. This band is assigned to bridged ν_{Rh-Cl}. Both the complexes are non conducting in nitrobenzene, diamagnetic and air stable. The diamagnetism of complexes indicates the oxidation of rhodium is either +1 or +3. The values of ν_{NS} (1120 cm^{-1}) are in the range which has been reported for terminal bent coordinated thionitrosyl group [10] .

Both the complexes I and II are soluble in benzene, dichloromethane, chloroform and insoluble in petroleum ether and hexane.

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CHAPTER II

THIONITROSYL COMPLEXES OF RHODIUM(III)

It has been known for many years that nitricoxide can coordinate to transition metals in a wide range of oxidation states to form metal nitrosyl [1,2]. Analogous thionitrosyl complexes are markedly less abundant, a fact which reflects primarily the present lack of reagents which can be utiliged to introduce the thionitrosyl group into a transition metal. Chatt, et.al. have reported the syntheses of thionitrosyl complexes of molybdenum, rhenium and osmium, containing linear thionitrosyl group [3-5] and Legzdins, et.al. orgonomatallic thionitrosyl complexes of chromium containing linear thionitrosyl group [6-8] we have reported the thionitrosy complexes of Ruthenium(II), Osmium(II), Rhodium(III) and Iridium(III), having three principal modes of bonding linear, bent or bridged , by the reaction of trithiazyltrichloride, which acts as a solvated monomer in THF or CCl_4-$CHCl_3$ [9-13]. This chapter describes the syntheses of thionitrosyl complexes of rhodium(III) by the reaction of hydridotetrakis (triphenyl-phosphine) rhodium(I) with trithiazyltrichloride in CCl_4-$CHCl_3$ mixture. These compounds have been characterized by various physico chemical methods and their geometries have been proposed.

EXPERIMENTAL

All the reagents used were of analar or chemically pure grade. All the solvents were dried and freshly distilled before use. The preparations were performed under the atmosphere of argon.

Hydridotetrakis(triphenylphosphine) rhodium(I) and trithiazyl-trichloride were prepared according to the methods described in the literature [14,15] .

Preparation of Complexes

$[Rh(NS)Cl_2(PPh_3)]_2$

A yellow solution of $(NSCl)_3$ in CCl_4 (20 ml) was added dropwise to a stirred solution of $[RhH(CO)(PPh_3)_3]$ (0.2g) in $CHCl_3$ at room temperature. The mixture was stirred for 1h more followed by evaporation of solvent under reduced pressure. The residue was extracted in benzene. On adding petroleum ether to the benzene extract, a brown compound $[Rh(NS)Cl_2(PPh_3)]_2$ (m.p. 215°C) was precipitated which was centrifuged out and washed with petroleum ether and water and dried in air. It was recrystallized from benzene-petroleum ether (1:3). Similar result was observed by using tetrahydrofuran inplace of CCl_4-$CHCl_3$.

Table II.1. Analytical data, melting points, colours and i.r. frequencies of the complexes

Compound	m.p. (^{o}C)	Colour	Found (calcd) C	Analyses H	N	S	Cl	Rh	P	I.R. frequencies (cm^{-1}) ν_{NS}
$[Rh(NS)Cl_2(PPh_3)]_2$	215	Brown	44.7 (44.8)	3.3 (3.1)	3.0 (2.9)	6.8 (6.6)	14.9 (14.7)	21.1 (21.3)	6.4 (6.4)	1118
$[Rh(NS)Cl_2(PPh_3)_2]$	160-163	Reddish brown	58.2 (58.0)	4.1 (4.0)	2.1 (1.9)	4.0 (4.3)	9.8 (9.5)	13.6 (13.8)	8.2 (8.3)	1120